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Follow-Up Study of the Distribution and Fate of Polychlorinated Biphenyls and Benzenes in Soil and Ground Water Samples After an Accidental Spill of Transformer Fluid

(U.S.) Environmental Protection Agency, Atlanta, GA. Region IV

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PB 288484

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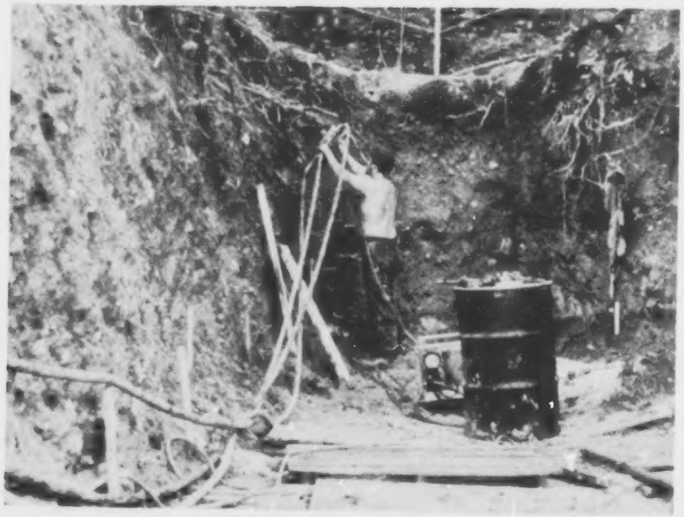

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OFFICE OF WATER PROGRAM OPERATIONS
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THIS TECHNICALLY ORIENTED STUDY WAS DESIGNED TO DERIVE A PCB CONCENTRATION PROFILE IN A SPILL AREA TWO YEARS AFTER THE OCCURRANCE OF THE SPILL. MANY MONTHS OF FIELD WORK AND LABORATORY ANALYSIS WERE SPENT TO EXAMINE NUMEROUS ENVIRONMENTAL FACTORS TO DETERMINE THE FATE OF PCB AND BENZENES IN THE NATURAL ENVIRONMENT. THE AREA, UNDER INVESTIGATION FOR MIGRATION AND/OR DEGRADATION WAS FOUND VIRTUALLY UNCHANGED WHILE THE SOLVENT HAD CONTINUED TO LEACH INTO THE ~~GROUND WATE~~ UNDERGROUND WATER. THERE WAS HOWEVER, NO EVIDENCE OF PERMANENT ENVIRONMENTAL DAMAGE DETECTED IN THE SPILL AREA

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FOLLOW-UP STUDY OF THE DISTRIBUTION AND FATE OF POLYCHLORINATED BIPHENYLS AND BENZENES IN SOIL AND GROUND WATER SAMPLES AFTER AN ACCIDENTAL SPILL OF TRANSFORMER FLUID

CONTRACT NO.: 68-01-3232

DIVISION OF OIL AND SPECIAL MATERIALS CONTROL
OFFICE OF WATER PROGRAM OPERATIONS
U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

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ATLANTA, GEORGIA

JANUARY, 1976

FOREWORD

The Environmental Protection Agency's interest in the spills of Polychlorinated Biphenyls (PCB) and related substances has been demonstrated through a series of response oriented actions, and joint EPA industry efforts to mitigate the damages caused by such spills. In recent years some significant quantities of PCB have spilled, mostly from transportation related media in remote and populated areas of the United States. In the Southeastern United States several such spills have occurred during the past three years causing alarm to the public and large clean up expenses to the industry.

This technically oriented study was designed to derive a PCB concentration profile in a spill area two years after the occurrence of the spill. This study is somewhat unique, in that many months of field work and laboratory analysis were spent to examine numerous environmental factors and parameters to determine the fate of PCB and Benzenes in the "natural environment". The findings and conclusions of this study should have significant value to EPA response personnel who often have to determine and recommend a "safe level" of clean up and removal operation; to the industry who frequently pays for such operations; and to the general public who is ultimately affected by the menace of spills. The tabular data contained herein are arranged as such that little interpretation is needed for understanding by laymen. Many diagrams, maps, and chromatograms have been included as supporting documentation and as reference for any future work.

Many individuals have contributed to the success of this project and should be acknowledged. Notably among them are Mr. Al J. Smith, Chief, Environmental Emergency Branch of EPA, Region IV, who directed the clean up and removal operation during the initial phases of the spill and coordinated the Federal response activities; Mr. Kenneth E. Biglane, Director, Oil and Special Materials Control Division, EPA, Washington, who conceived the idea for the follow-up study and provided the necessary funding; Messrs. Bill Loy and Tom Bennett of Surveillance and Analysis Division, EPA, Region IV, who assisted in the sample analysis and the quality control phase.

It is reasonable to expect that subsequent studies of a more detailed nature will be made in this area to answer many remaining questions.

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I. SUMMARY

The area of an askarel spill, which had been cleaned up two years prior to this study, was investigated for migration and/or degradation of residual PCB and lingering intrusion of the solvent into ground waters. The PCB was found unchanged while the solvent had continued to leach into the underground water.

II. CONCLUSIONS

No significant reduction in the concentration of Aroclor 1254 in the soil has occurred as the result of migration or degradation. There is no way to clearly assess the effect of the original insult on the soil microorganism population of the spill site since no microbiological studies were conducted in 1973. There was, however, no evidence of permanent environmental damage detected in the spill area in 1975.

The more water-soluble components of the askarel solvent invaded the ground water supply almost immediately after the occurrence of the spill. Leaching was the migration mechanism responsible for the intrusion of the lower chlorinated benzenes into the ground water.

III. RECOMMENDATIONS

Because of the many diverse and interrelated effects imposed by a particular spill environment, no threshold concentration of PCBs can be recommended which would be equally applicable to all land spill occurrences. Although the data from this study can serve as a guideline, each PCB spill will require an individual evaluation and assessment since no appreciable migration or degradation was detected in the specific environment investigated. It is recommended that more research be conducted with varying soil types and a more favorable medium for sustaining microorganisms in greater abundance. More knowledge of the toxicity of askarel on various microbia would be required as an integral part of these degradation studies.

IV. INTRODUCTION

A. History of Spill.

On March 5, 1973, an accidental spill of approximately 1500 gallons of askarel occurred in a rural area near Kingston, Tennessee. The spill resulted in the environmental contamination of two watersheds because of its location on the crest of a hill. Through the influence of rainfall, geology, and characteristics of the overlying stratum of soil, the chemical was subsequently dispersed through the soil both horizontally and vertically.

The particular askarel spilled was composed of a commercial mixture of polychlorinated biphenyls (Aroclor 1254) and a proprietary solvent mixture of polychlorinated benzenes. Both components of the askarel involved were chlorinated hydrocarbons --a class of compounds noted for their persistence in the environment. Consequently, an extensive "clean-up" operation in the affected area was started March 14, 1973, by the responsible parties. To assure the effective removal and proper disposal of the hazardous substances, the contaminated soil was packed and sealed in metal drums before it was taken from the spill site. The removal procedure resulted in extensive excavations in three general areas. After 11,531 drums of contaminated soil were removed, the excavated areas were sealed, backfilled, and packed with uncontaminated soil. The entire affected area was subsequently covered with top soil, seeded with grass, and landscaped.

On March 8, 1973, the Regional Office (Region IV) of the Environmental Protection Agency (EPA) in Atlanta commenced a sampling program of the affected areas to determine the concentration level of contaminants in the soil and water table. Stewart Laboratories, Inc. (SLI), a private laboratory located in Knoxville, TN, joined EPA in the sampling program on March 21, 1973. This sampling program, for monitoring and detection purposes, continued jointly by EPA and SLI for several additional weeks. In addition to the EPA sampling program, Stewart Laboratories provided sampling and analytical assistance during the excavation.

A monitoring program, approved jointly by EPA and TWQC (Tenn. Water Quality Control Board) was conducted for a 12-month period following the cleanup operation.

B. Brief Review of PCB Literature.

1. Distribution of PCBs in the Environment. According to the Interdepartmental Task Force on PCBs (1), the history of PCBs started in 1929 when industry introduced them for use as non-flammable oils in electrical transformers, condensers, and in paint. During the next forty years, industrial uses of PCBs grew steadily. They have been widely employed as plasticizers, as sealers in waterproofing compounds and putty, in printing inks, in waxes, in synthetic adhesives,

in cutting oils, as dielectrics, as hydraulic fluids, as high-pressure lubricants, and as a heat-transfer medium (2). Sales of PCBs in the United States came to about 34,000 tons in 1970, with cumulative production over the years amounting to an estimated 4 x 10^5 tons (3).

Although PCBs were never intended for direct release into the environment, they were first identified by Jensen as a potential food contaminant in 1966 (4). Since that time, it has been demonstrated that they are ubiquitous environmental pollutants. Numerous studies (5-18) have confirmed their presence in animals and the aquatic environments as well as in humans.

2. Fate of PCBs in the Environment. The sparsity of knowledge about the fate of PCBs in the environment is illustrated by the recommendation of the Interdepartmental Task Force on PCBs (1) that "more scientific information about PCBs is needed" relative to their occurrence, transfer, and cycling in the environment. Only general statements can be made about how PCBs reach the environment and how they reach target organisms.

The biologically important characteristics of PCBs are their insolubility in water, high solubility in fats, toxicity to metabolic processes, and extreme stability. The combination of persistence and accumulation in fat (during transition through a food chain) can result in considerable increases in concentration of the compounds at higher levels in the food chain. Like DDT, PCBs are reported to degrade very slowly under natural conditions (19). The highly chlorinated PCBs (Aroclor 1254 and 1260) seem to persist in the environment longer and are less toxic than the more rapidly degradable low chlorine forms (20).

The metabolism of several PCB isomers in fish, rats, and pigeons has been studied by Hutzinger and co-workers (21). Mono-, di-, and tetrachlorobiphenyl isomers were converted into their corresponding mono-hydroxy derivatives in rats and pigeons. However, no hydroxylation of any of the isomers was observed with fish. It was also observed that 2,2',4,4', 5,5'-hexachlorobiphenyl was not oxidized by any of the animals in the study.

Laboratory photolysis studies on pure chlorobiphenyl isomers, as well as Aroclor 1254, have been reported by a number of investigators (22-26). Using hexane as the solvent, the dechlorination reaction was predominant. However, in the presence of air and water, a number of polar products were observed. Examination of the polar products from the Aroclor 1254 irradiation indicated formation of both hydroxylated and hydrated products. Although these results suggested pathways in which degradation of environmental PCB might occur, the actual observation of degradation products in "natural environmentally aged samples" has not been reported to date.

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C. Purpose of This Study.

The primary purpose of this project is to study the biodegradation effects of a natural environment on the chemical components of an askarel spill after a two-year time lapse. Extensive experimental background data were obtained during and after the 1973 cleanup procedures employed at the study site. Correlation of the 1973 data with the results of this follow-up study will provide a means of assessing the distribution and fate of PCBs and polychlorinated benzenes in natural environmentally aged samples.

The findings of this project may form the basis for deriving a safe concentration level for PCBs in soil. The practical application of such a threshold level will assist EPA spill response personnel to determine the degree of soil removal necessary in a land spill situation. Sampling of water supplies adjacent to the spill area will provide information on the rate of intrusion of lower chlorinated benzenes into ground water. Such information will be of paramount importance in increasing the efficiency and effectiveness of EPA's spill cleanup efforts.

V. TECHNICAL APPROACH

A. Introduction.

Potential mechanisms for the loss of askarel from the spill site include volatilization, leaching, and metabolic and/or nonmetabolic degradation. The experimental approach to be employed in this study has been designed in a manner which will detect and assess the magnitude of each potential route for the removal of residual askarel from the spill site.

Data obtained by Stewart Laboratories, Inc., during the 1973 site cleanup included: (1) core samples in the bottom of excavation areas immediately prior to fill; (2) core samples at elevations geologically below the spill; (3) water and sediment samples from a spring well in a watershed below the site; (4) water samples from domestic wells adjacent and peripheral to the spill area; (5) water samples from sources in the general vicinity of the spill area; and (6) water samples from a domestic control well. The initial phase of this project involved a re-sampling of the area in order to determine migration and/or degradation of the PCBs in soil and askarel concentration changes in water.

The second phase of the study provided the analytical data necessary to evaluate any changes which might have occurred over the past two years. Identical analysis procedures, concentration units, and detection limits were employed for the determination of PCB content in both the present study and the 1973 project so that direct comparison of the two sets of data would be facilitated. Careful choices were made as to which samples should be confirmed and identified by GC/MS analysis. The requested isomer identifications were done by the Surveillance and Analysis Division, Region IV, EPA, in Athens, Georgia. The techniques employed in the field and laboratory positively identified soil profile correlations which allowed for the interpretation of chemical and biological data.

Core samples of soil were examined by established procedures to determine the relative numbers and major types of microbial flora. Among these were the true bacteria, actinomycetes, and a wide variety of microscopic fungi, all of which were enumerated and identified.

Algae and protozooans are also found in soil. However, they are far less numerous than the other microorganisms (27) and are more difficult to evaluate because of somewhat unique cultural requirements and were, therefore, not investigated.

Since available literature indicates that very little is known concerning the degradation of PCBs in the natural environment, potential biodegradative microorganisms are not identifiable. The two-year lapse since the spill incident, however, should have allowed for some valid degradation. The over-all approach in determining microorganism abundance was to isolate certain groups which were probable major participants in chemical alterations. It was realized, however, that other environmental conditions such as pH, moisture, type of soil, and sample depth influence the relative numbers and varieties of soil flora.

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B. Sampling Protocol and Collections.

During the field sampling phase of the project, the contractor collected 120 soil samples and 40 water samples in and around the spill area. These samples were to constitute the basic materials for the study of the distribution and fate of residual PCBs in the natural environment. Probable causes of measured and documented changes in the chemical status of the spill components could then be addressed.

An initial over-all assessment was made of the requirements for proper choice of primary sampling sites, procedures for collection of samples and attendant field data, as well as essential equipment and supplies. A final protocol was established which required only minor modifications once the field work began.

1. Criteria for Selection of Soil Sampling Sites. All analytical data obtained should have reasonable reference to analyses performed in 1973. The core sites chosen for comparison were to represent a broad concentration range. The areas from which these cores were taken needed to exhibit a full spectrum of topographic variables which would characterize the study area as to soil type, probable hydrology, microbial environments, and potential migration of PCBs. Attempts needed to be made to sample areas of undisturbed terrain as well as those which had been excavated or top dressed in 1973. Distribution patterns of the residual contamination in the 1973 cores were studied in order to replicate, as closely as possible, the same contamination variability for the 1975 sampling. The depth of sample takes would be dependent on the assessment of all other criteria thus mentioned. It would, therefore, be essential that an appropriate number of available sites be chosen so that the interdependency of all these requirements could be upheld; and unforeseen field situations would not preclude an adequate sampling.

2. Initial Field Preparations. The spill area had received little maintenance since it had been backfilled and seeded in 1973. Successive cuttings with rotary mowers and hand raking were required to remove grass, weeds, and limbs from the study area. Photographs, drawings, and field data were

used to approximate the location of the excavation perimeter and the 1973 core sites. Surveyors' flags and stakes were used to mark these assigned areas. Photographs and rough sketches were recorded as guides for final and more exact designation.

3. Drilling and Soil Sampling. The extreme variability in depth of required cores and the soil matrix (clay with fractured quartz) indigenous to the site area required the use of a truck-mounted drill rig. The drill unit was thoroughly washed and cleaned prior to arrival on site. It remained in the study area throughout the sampling period.

A methodical drilling program was begun to determine the excavation limits in all areas peripheral to probable sampling sites. Continuous cores were pulled using a split spoon sampler for the determination of soil profiles. Since the floor of all excavated areas had been sealed with "Visqueen" and a layer of sand (2-4 inches) prior to backfilling, the position of the perimeter of the disturbed area was readily discernible. Appropriate adjustments on all drawings and records were made as documentation. All field markers were securely installed at their verified locations. During this preliminary drilling period, extreme precautions were taken against contamination of the surface of the study areas. The positioning of the drill truck and the disposition of the test cores were under constant surveillance. Once logging of core data was completed, the cores were tamped back in their original holes.

All original 1973 core sites external to the excavation had been backfilled, packed, and covered with top soil. In order to identify the core holes and differentiate fill top soil from natural overburden, each core hole was found and drilled once with the split spoon. By visual observation and actual measurement of the soil strata, the depth of unnatural cover material was ascertained. The sampler was pressed gently and rotated in order to avoid compacting. Impact techniques were restricted to instances where chert refused penetration.

Available core sampling equipment included a split spoon sampler, a Shelby Tube Sampler, and a California Sampler. The order of desirability of the three core samplers were:

a. California sampler--consists of four sequential brass units two inches in diameter and four inches long allowing for ease of sample removal and differential choice of sample take. The cost per tube is moderate and they are readily available. Two limitations were the questionability of penetration of quartz layers and the sample size.

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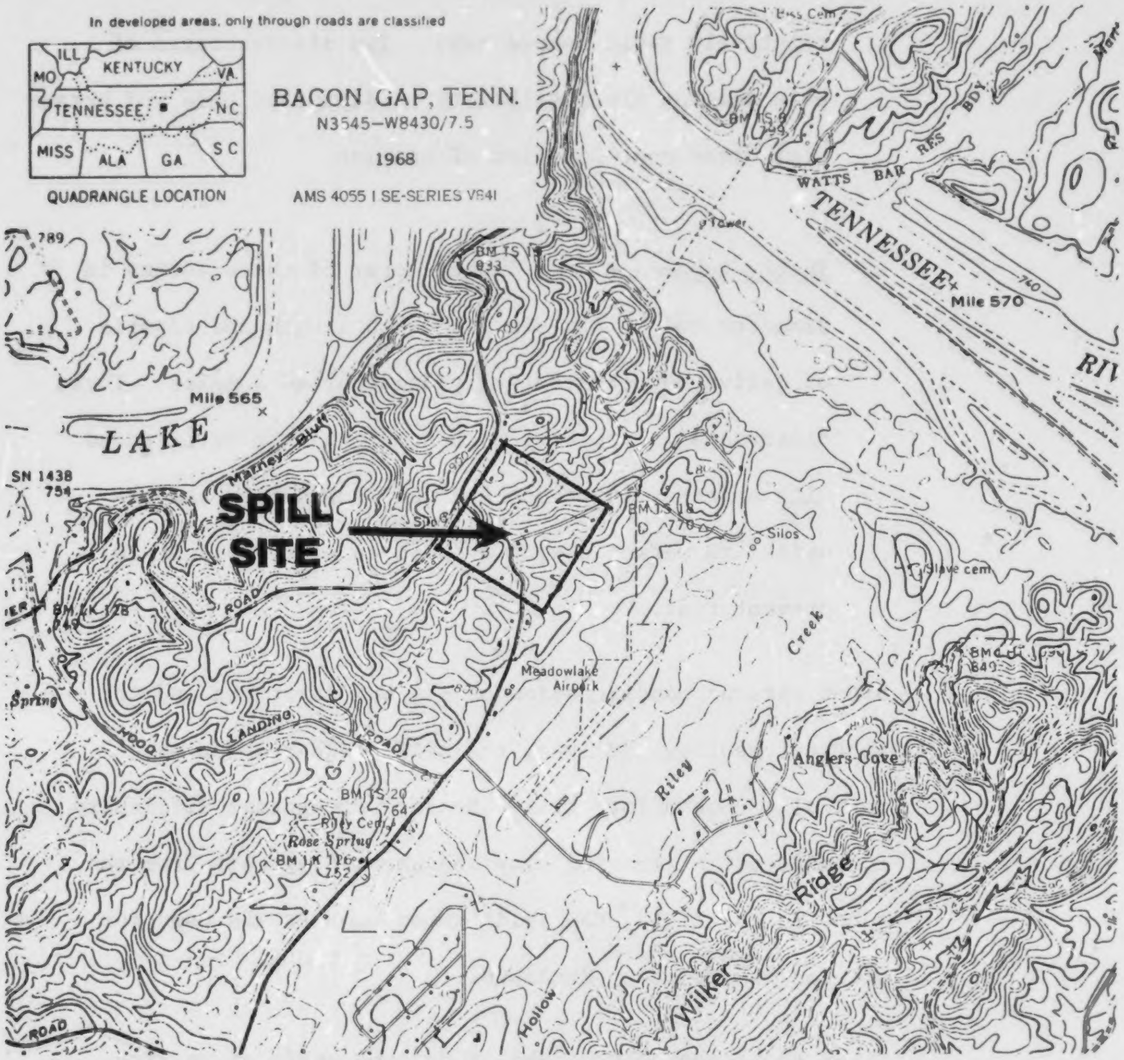
ROAD CLASSIFICATION

Heavy-duty	Poor motor road
Medium-duty	Wagon and jeep track
Light-duty	Foot trail

In developed areas, only through roads are classified

EXHIBIT I Location of Spill Site in Relation to General Topography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Wilker Ridge
ROAD
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QUADRANGLE LOCATION

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1968
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SCALE 1:24 000

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CONTOUR INTERVAL 20 FEET
DASHED LINES REPRESENT HALF INTERVAL CONTOURS
DATUM IS MEAN SEA LEVEL

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A FOLDER DESCRIBING TOPOGRAPHIC MAPS AND SYMBOLS IS AVAILABLE ON REQUEST

b. Split spoon sampler--an open-chambered tube two inches in diameter and ∿24 inches long which provides a relatively rapid sample take. Two disadvantages of this sampler are possibility of disturbed core and potential cross contamination of samples.

c. Shelby tube--a sturdy impact corer of three inches in diameter and thirty-six inches in length and capable of delivering substantially undisturbed samples. Three disadvantages are that each sample has to be extruded with a press, the tubes are very expensive, and the units are marketed with a baked-on plastic liner to prevent rust.

After careful consideration of the sampler types and the inherent geology involved, the California Sampler was initially chosen for trial. Because of extreme difficulty encountered in removing clay and chert fragments from the tubes in the field, the split spoon sampler was used for all consequent core samplings.

Since the topography of the study area rolls at varying angles around the spill site, a fairly comprehensive choice of sampling spots was made. The Knox Dolomite (undivided) sub-surface versus the overburden influx on some of the sites external to the excavation broadened the coverage of the study region from the standpoint of degradation and/or movement of PCBs. A topographic representation of the general spill site is shown in Exhibit I.

Sample core drilling began on August 4, 1975. The first three core sites chosen for replicate testing were drilled in a four-cornered quadrant pattern. Each of the four cores was taken approximately one foot from the center of the 1973 core location. All samples were taken over four-inch intervals to allow for differentiation of gradient effects and reproducibility studies.

In order to representatively sample the site variations as specified in the protocol, all subsequent collections were designed to take soil from one core hole adjacent to an identified 1973 core hole. This phase of collections began with core taken over four-inch intervals; however, sampler refusal and tendency toward loss of sample integrity because of inherent quartz in the clay matrix precluded sampling over such a short interval. A decision was made to complete the sampling with cores composited over sixteen-inch intervals.

Upon completion of all collections peripheral to the excavation area, core samples were taken at a level approximating some of the original sample points at the bottom of the backfilled areas. The location of these samples was confined to an area within three feet of the 1973 sampling point. Few sites were available for this phase of the study since nearly all excavation areas received additional cleanups after final data had been obtained in 1973. Additionally, the floor and walls of one deeply excavated area had been impregnated with a material to inhibit movement of any residual askarel. There was no ready access to the basin sampling areas without breaking the seal to the environment.

4. Field Procedures Relating to Soil Sampling. The techniques employed in the actual sampling and handling of core samples and the collection of supplemental field data followed the protocol with no modifications.

   a. Core samples--Each split spoon sample was carefully removed onto a piece of aluminum foil supported on a plywood base. It was measured, cut into four sections of four-inch length, logged, characterized as to general soil type, and sealed in labeled foil for transport to the laboratory.

   b. Cleaning and contamination precautions--Prior to each use, all drilling equipment, core cutting blades, etc., were washed with water and a brush, scrubbed in a bath of technical grade hexane, and finally rinsed in pesticide grade hexane. This operation was not performed near sampling sites. Disposable gloves were used while handling each sample take, and all throw-away materials were kept carefully sealed. Foil strips were removed from the roll and appropriately labeled in an area remote to the core operations.

c. Temperature measurements--A general profile was made of the temperature of the soil at several points within the study area. A four-inch temperature-sensing probe with a strip chart recorder readout was inserted in the test cores. Cross checks on the accuracy of these readings were made by inserting the probe in soil at verying depths in advance of core takes. General confirmation between these two procedures was obtained. The probe was cleaned in the manner described in "b" above.

d. Mapping--A grid survey on two-foot intervals was made of the entire study area. The data from these measurements were translated into a contour map depicting the exact location of sampling sites and excavation limits on a grid basis. Substantiating photographs were shot over the entire region with identifying landmarks in plain view.

e. Restoration--A concerted effort was made to return the area back to its original state. All core holes were plugged; stakes, flags, and twine were removed; and all equipment, tools, and supplies were returned to the laboratory facility.

5. Site Selections for Sediment and Water. A protected spring well located in the watershed below the spill site had been monitored during the 1973 cleanup and subsequently for about a year. Since some positive data had been obtained from the spring as late as May 1974, the well was chosen as an indicator site of extensive ground water movement.

Below the spring well, a creek drains the immediate spill area and then enters an impoundment. The mouth of this creek was sampled in order to determine if there was surface contamination movement from unknown sources.

The well stations considered to be of prime interest in this study were those located adjacent to and/or at an elevation lower than the excavation area. Five of the seven study wells were monitored in 1973-74 and, therefore, represent stations with an extensive analytical data base. One well, station 89, is completely removed from the spill site and represents a control used in 1973-74.

6. Sampling Procedures for Sediments, Water, and Controls. Once the sites external to the spill were chosen and collection permission obtained from the well owners, grab samples were taken after relatively dry weather (August 29, 1975) and again after heavy rains (September 26, 1975).

a. Techniques--Sediments were taken with a metal, roll-sided scoop since the depth of water was quite shallow. Each sample was placed in a pre-labeled glass jar whose cap was lined with aluminum foil.

All water samples were taken directly into a pre-labeled gallon glass jug. Well samples were obtained at the tap from which they had previously been sampled in 1973. Each tap line was allowed to flush for 2-3 minutes so that samples could be drawn directly from the well system itself.

Two control soil samples were taken from nearby areas not influenced by the spill. The collections were made at 3-6 inch depths below the surface. One of these was from an exposed clay and chert matrix while the other was primarily loam.

b. Cleaning and contamination precautions--The sediment scoop was cleaned according to the procedure previously given for field equipment. All glass containers were washed with distilled water, rinsed with technical grade hexane, rerinsed with pesticide grade hexane, capped with foil liners, and labeled at the laboratory. Special care was taken to insure that caps and glass container mouths did not come into contact with potential contaminants in the field.

C. Preliminary Laboratory Preparations and Splits of Soil Samples.

Sediments were passed through a quarter-inch screen in order to remove inorganic and organic debris. These samples were allowed to air dry in a metal tray. The dried material was then passed through a U. S. Standard No. 18 sieve to insure uniformity of particle size. The sediments were then submitted to the laboratory for PCB analysis.

Core samples were mixed and spread for air drying on their individual aluminum foil sheets. As the samples were being spread, an approximate 40-gram sample for moisture, pH, and microbiological determinations was sealed in a pre-labeled container and submitted for analysis. Forty representative soil samples of approximately 100 grams each were sealed in containers for potential subsequent anaerobic study.

The dried core aliquots for PCB determinations were passed through a U. S. Standard No. 18 sieve after obvious rocks and debris had been removed. The fines were then passed through a splitter in order to obtain an aliquot of an appropriate size for analysis. This aliquot was submitted to the laboratory for analysis of PCBs.

All sample preparations were performed under clean room conditions. Disposable gloves were worn and all equipment and containers were pre-cleaned by washing and subsequent hexane rinses. Samples were kept distinct from each other, and each step of the preparations was done in a separately ventilated zone in the laboratory.

D. Microbiological Studies.

One hundred forty-two soil samples were examined to determine the populations of heterotrophic aerobic bacteria, fungi, and actinomycetes, which constitute the majority of microorganisms in soil. Laboratory data concerned with microbial flora enumeration and identification were researched in correlation with soil type, pH, moisture, and sample depth.

1. Procedures for Microorganism Investigations. The various techniques and culture media described by Parkinson, et al. (28) were used for the isolation of the soil microorganisms.

Ten grams of each soil sample were suspended in 95 ml of sterile distilled water to give a 1:10 dilution. From this, serial 10-fold dilutions were prepared. Dilutions of 1:100 through 1:1,000,000 were employed for determining plate counts to enumerate the three microbial groups. The numbers of heterotrophic aerobic bacteria were obtained by plating the various dilutions of the soil samples in Plate Count Agar (Difco Laboratories, Detroit, Mich.) and incubating at 25°C for 72 hours. Colony counts were then determined with the use of a Quebec Colony Counter (American Optical Company, Buffalo, N. Y.). Determination of fungal counts were conducted by plating dilutions of the samples in Sabouraud's Dextrose Agar (Baltimore Biological Laboratories, Cockeysville, Md.) with incubation at 25°C for 96-120 hours. Enumeration of the organisms was performed as described for the heterotrophic bacteria. Actinomycete counts were made by plating soil dilutions in Starch Casein Agar containing 0.0002 percent actidione for inhibition of fungi (Kuster and Williams, 1964), followed by incubation at 25°C for 96-120 hours. Again, colony counts were made after incubation as described above. If no growth was observed on the fungal or actinomycete plates after 96 hours, incubation was continued and the plates read at 120 hours in order to detect any slower growing organisms. The heterotrophic aerobic bacteria grew readily and never required more than 72 hours for maximum growth.

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(28) Methods for Study the Ecology of Soil Microorganisms. 1971. D. Parkinson, T. R. Gray, and S. T. Williams. International Biological Programme Bladswell Scientific Publications, Oxford, England.

2. Determinations of Soil pH and Moisture.

The pH of each sample was obtained by preparing a slurry with three grams of soil and three ml of distilled water in a 10 ml beaker and making the determination with a Labomatic Model 165 pH meter.

Moisture content of a representative five-gram aliquot of each sample was obtained by drying to constant weight at 110°C.

E. Analytical Methodology.

The method of choice for the analysis of PCBs in all known monitoring and regulatory applications is GC/EC (gas-liquid chromatography utilizing electron capture detection). This analysis mode is, likewise, most frequently employed in the assessment of the environmental impact and health effects of PCBs. This overwhelming utilization is by no means intended to imply that the analytical method is the ideal mode of analysis for PCBs. Gas chromatography is not an inherently definitive analytical technique. It is subject to serious complications when other electron-capturing components are present in the samples in addition to the PCBs. The shortcomings of the method can be successfully overcome when the analyst involved is fully cognizant of the ramifications of the situation. Most analytical techniques incorporate a liquid chromatography cleanup of liquid-liquid extracts prior to GC/MS (gas chromatography/mass spectrometry) analysis. This procedure is ∿ 90 percent effective in separating PCBs from organochlorine pesticides.

The utilization of two or more unlike columns in the gas chromatographic analysis is another means for establishing the identity of gas chromatographic patterns. The application of GC/MS is considered by most experts to be the desired technique for confirming qualitative identification of gas chromatographic patterns. Microcoulometry and thin layer chromatography are also useful tools for positive identifications. It is appropriate to conclude, however, that GC/EC is a most effective analysis mode for the detection and measurement of PCBs in environmental samples when interfering substances are either totally absent from the samples under study or when they have been effectively removed prior to analysis.

1. Analysis of Water, Sediment, and Soil for Polychlorinated Biphenyls (PCBs).

a. Background information--Since this project is a follow-up study and many conclusions will be based on correlation of current analytical data with that obtained at the time of the spill (1973), a consentaneous decision was made by all responsible parties that the GC/EC analytical methodology should not change from that employed in 1973.

The method employed in 1973 for the analysis of water, sediments, and soils for PCBs is basically the method from the R & D Laboratories of Monsanto Company (Method 69-13) which is contained in the publication Manual of Analytical Methods prepared by the Perrine Primate Research Laboratories of EPA (current designation: Pesticides and Toxic Substances Effects Laboratory, NERC, Research Triangle Park, N. C.). The contractor modified the Monsanto method to incorporate the Perrine column selection and instrumental recommendations. In principle, the contractor's method is unchanged from the Monsanto method. The PCBs in water, sediment, and soil are extracted into hexane. Interfering components, if present, are then removed from the extracts by chemical treatment and column adsorption chromatography. The amount of PCB present is determined by electron capture gas chromatography.

b. Analytical method--The complete Monsanto method constitutes the Appendix of this report, and only those pertinent modifications employed by the contractor will be discussed at this time. The chromatographic column used is the most significant change. The column packing is 1.5% SP 2250/1.95% SP 2401 on 80/100 mesh Supelcon AW-DMCS (Cat. #01-1947, Supelco, Inc.). This is a custom packing prepared to the Perrine Research Laboratories' specifications and is especially suitable for the separation of chlorinated pesticides and other chlorinated hydrocarbons. The gas chromatographic conditions employed for the analysis of Aroclor 1254 and method sensitivity data are contained in Tables 1 and 2, respectively. Typical chromatograms of Aroclor 1254 and the askarel involved in the 1973 spill are shown in Figures 1 and 2.

c. Operational narrative--

Concentration and chemical clean-up. After the initial liquid-liquid or liquid-solid extractions, exploratory chromatograms were run to determine whether the extracts would require further adjustment by dilution or concentration to bring the peaks into a quantifiable range consistent with the linear range of the detector. When these initial chromatograms indicated the presence of interfering materials, extensive clean-up procedures were employed. In most instances, the hexane extracts required no additional clean-up.

Contamination. To insure against the possibility of undetected contamination, blanks were routinely carried through all steps of the procedure.

Measurement. Initially, both the individual and total peak height methods were employed to determine the amount of Aroclor 1254 present. It was soon found, however, that a calibration plot of the major isomer peak height could be used for the quantitation of the Aroclor.

Table 1. Gas Chromatographic Operational Parameters - PCB's

Instrument: Beckman GC-45

DETECTOR: Electron Capture (polarized helium plasma)
Source Current: 7ma   Polarizing Voltage: 610 volts
Scavenger: He, CO_2, Rate 80, 1.2 ml/min.

GAS: Helium   Carrier Flow: 60 ml/min.

COLUMN: Glass   Length: 6 feet   Diameter: 1/4"

Coating: SP 2250/SP 2401   Conc.: 1.5%/1.95%

Support: Supelcon AW-DMCS   Mesh: 80/100

TEMPERATURE:

Column: 195°C   Injection Port: 220°C

Detector: 250°C   Detector Line: 240°C

SENSITIVITY: x 8 K   Recorder Range: 1 mv

CHART SPEED: 1/2 inch/minute

Table 2. Method Sensitivity - PCBs

Water: 0.5 parts per billion sensitivity

Absolute sensitivity = 0.1×10^{-9} grams

Volume injected = 6 µl

Final volume extract = 10 ml

Sample size = 1000 ml

Sediment: 0.05 parts per million sensitivity

Absolute sensitivity = 0.1×10^{-9} grams

Volume injected = 6 µl

Volume extract = 200 ml

Sample size = 100 grams

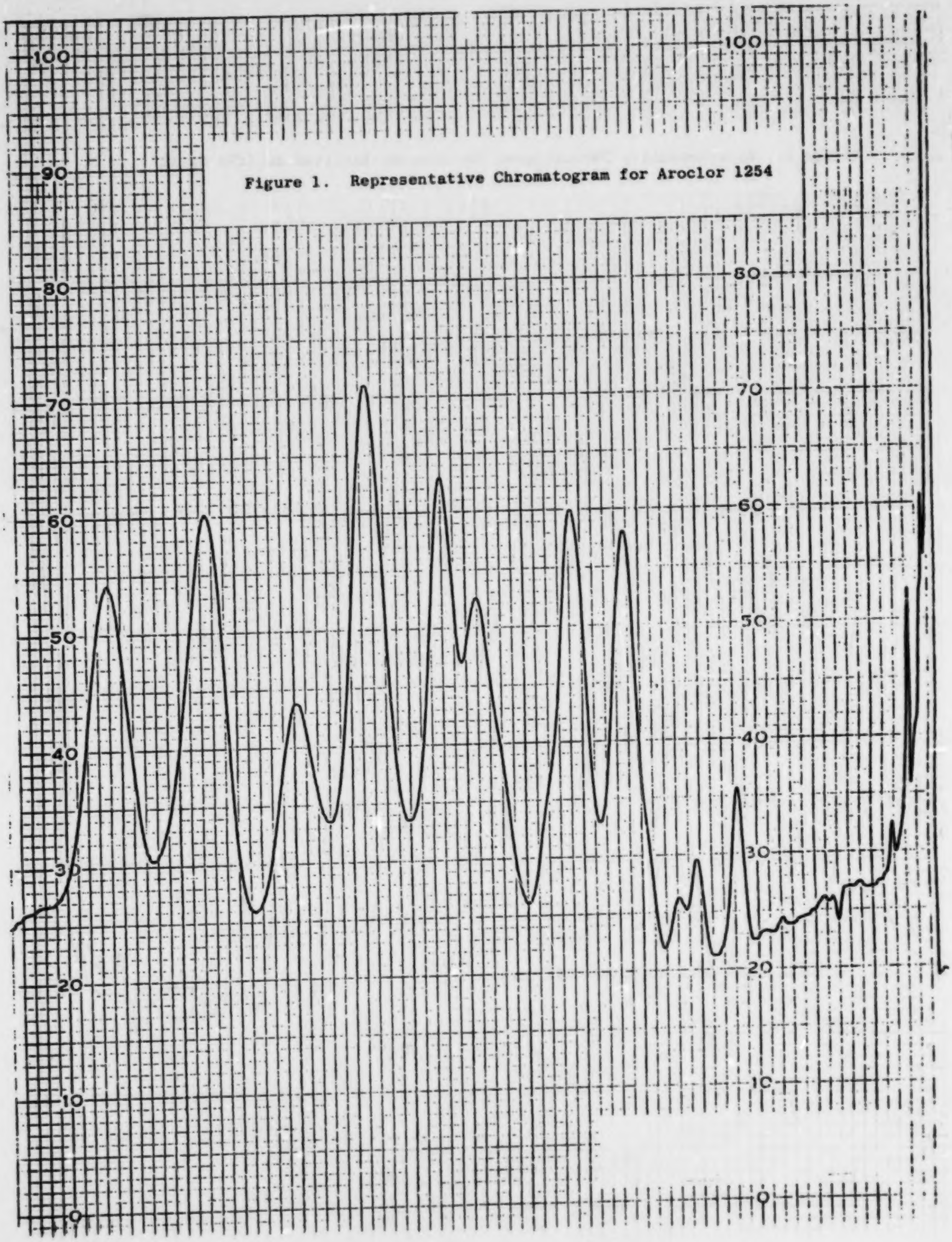
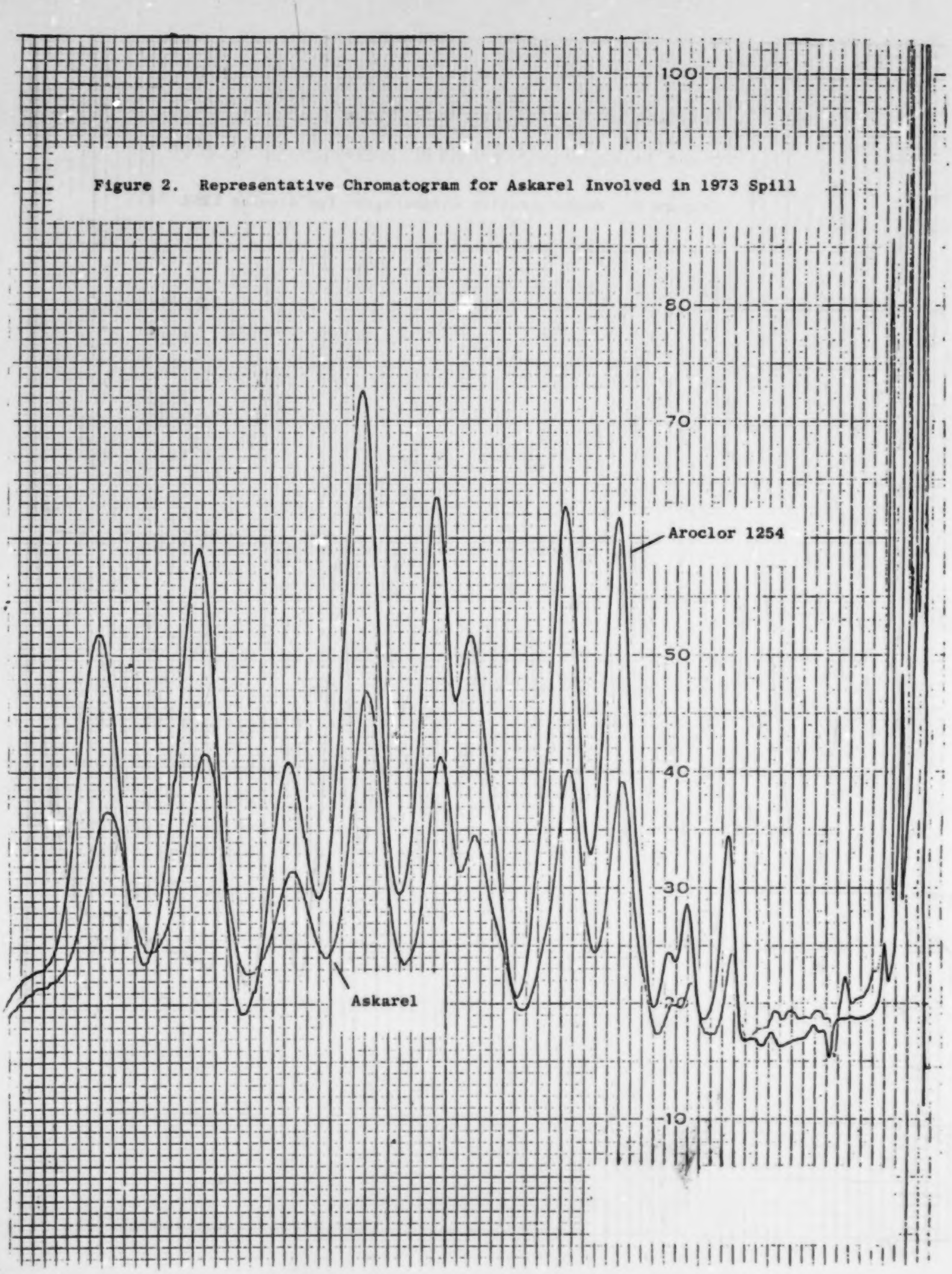


Figure 1. Representative Chromatogram for Aroclor 1254

Figure 2. Representative Chromatogram for Askarel Involved in 1973 Spill



Chlorinated Pesticide Interferences. Since surface water drainage of the area of interest was known to involve some agricultural land, a chromatogram showing the elution pattern of 13 of the more common chlorinated pesticides was run using the instrumental conditions of the Aroclor method. Pesticides in the mixture included α - BHC, β - BHC, Lindane, Heptachlor, Aldrin, Heptachlor Epoxide, p,p'-DDE, Dieldrin, Endrin, o,p'-DDD, p,p'-DDD, o-p'-DDT, and p,p'-DDT. The major isomer peak for Aroclor 1254 was free from interference from any of these pesticides under the analysis conditions employed.

2. *Analysis of Water, Sediment, and Soil for Polychlorobenzenes*.

a. *Background information*--Since the solvent for Aroclor 1254 in askarel is a mixture of chlorobenzenes, the fate of the solvent in the environment of the spill area needed to be determined. Because of chemical similarities between PCBs and the solvent components, the analytical method of choice was again electron capture gas chromatography.

b. *Analytical method*--The solubility of the solvent components in hexane made it possible for a solvent analysis to be performed on the same extract prepared for the

PCB analysis. Likewise, the versatility of the chromatographic column selected for the PCB analysis allowed for its use in the solvent analysis. Instrumental parameters for the solvent analysis are found in Table 3. Method sensitivity data are contained in Table 4. A chromatogram of the solvent portion of the askarel is shown in Figure 3. For reference, a chromatogram of a mixture of various chlorobenzenes is also included as Figure 4.

F. Isomer Verification.

The Surveillance and Analysis Division, Region IV, Environmental Protection Agency, Athens, Georgia, provided the identification and verification of PCB isomers in the natural environmentally aged samples using GC/MS.

Table 3. Gas Chromatographic Operational Parameters - Askarel Solvent

Instrument: Beckman GC-45

DETECTOR: Electron Capture (polarized helium plasma)
Source Current: 7 ma   Polarizing Voltage: 610 volts
Scavenger: He, CO_2, Rate 80, 1.2 ml/min.

GAS: Helium   Carrier Flow: 60 ml/min.

COLUMN: Glass   Length: 6 feet   Diameter: 1/4"
Coating: SP 2250/SP 2401   Conc.: 1.5%/1.95%
Support: Supelcon AW-DMCS   Mesh: 80/100

TEMPERATURE:
Column: 125°C   Injection Port: 220°C
Detector: 250°C   Detector Line: 240°C

SENSITIVITY: x 8 K   Recorder Range: 1 mv

CHART SPEED: 1/2 inch/minute

Table 4. Method Sensitivity - Askarel Solvent

Water: 0.006 parts per billion sensitivity

Absolute sensitivity = 0.003 x 10^{-9} grams

Volume injected = 6 µl

Final volume extract = 10 ml

Sample size = 1000 ml

Sediment: 0.010 parts per million sensitivity

Absolute sensitivity = 0.003 x 10^{-9} grams

Volume injected = 6 µl

Volume extract = 200 ml

Sample size = 100 grams

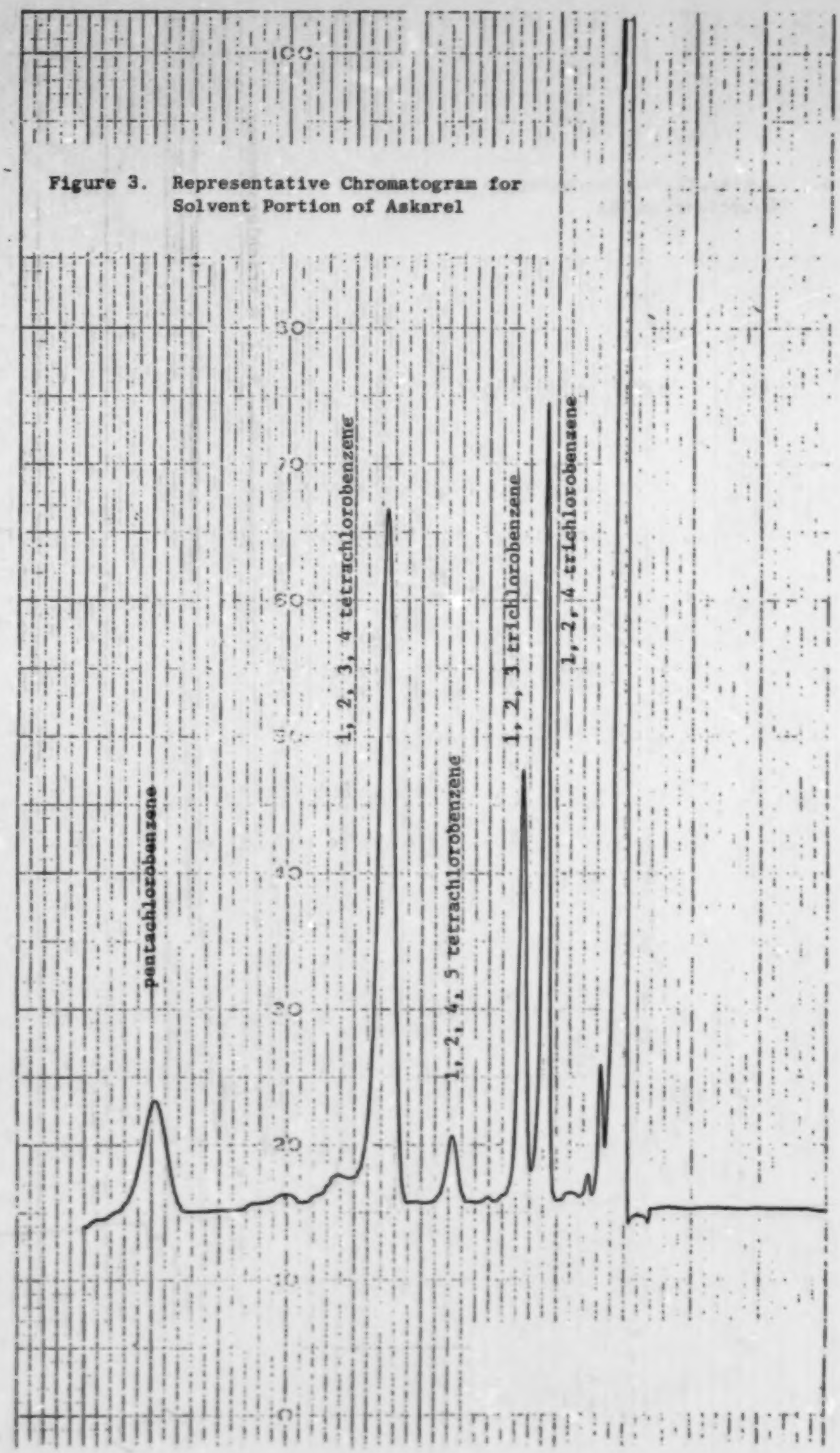


Figure 3. Representative Chromatogram for Solvent Portion of Askarel

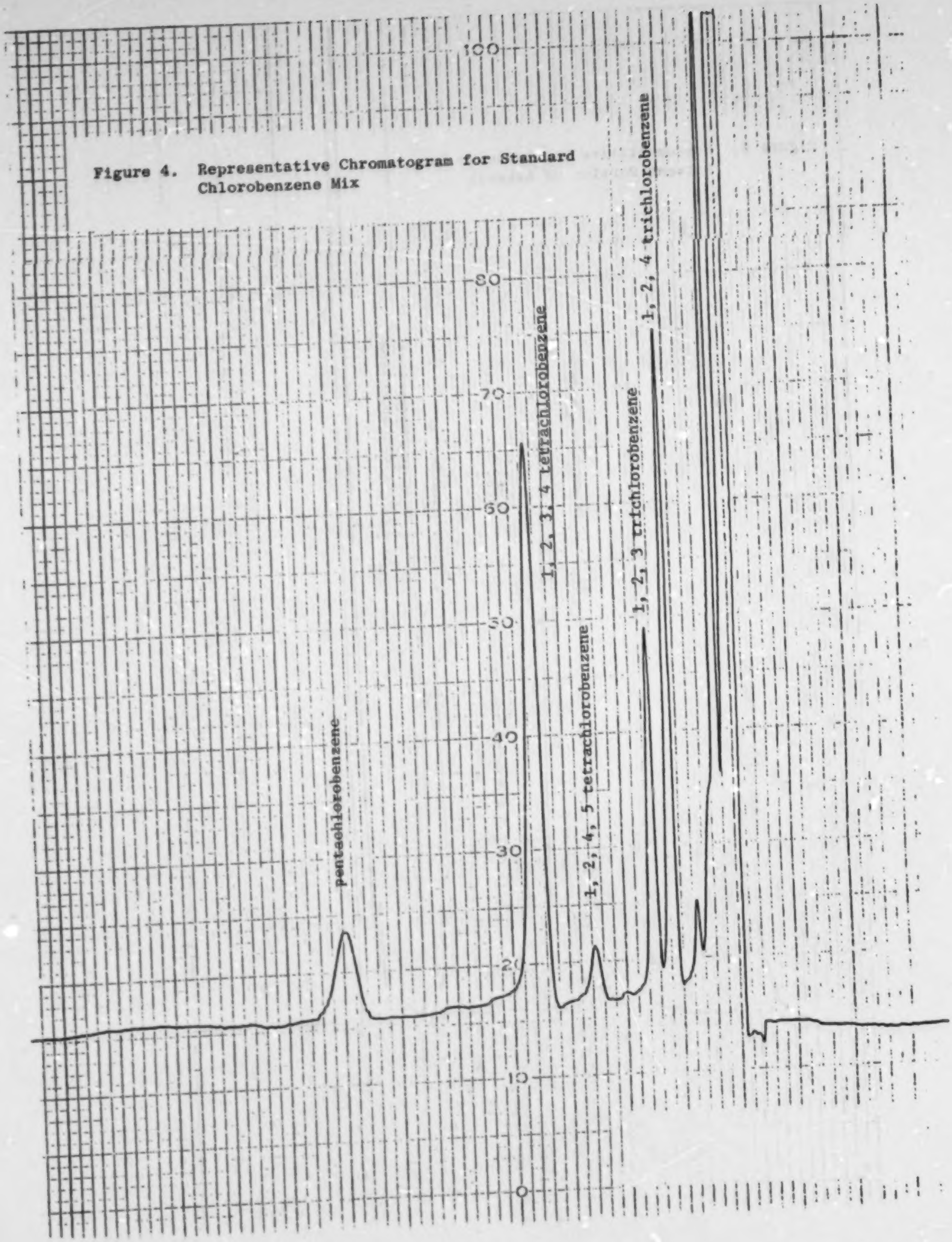


Figure 4. Representative Chromatogram for Standard Chlorobenzene Mix

VI. EXPERIMENTAL RESULTS

A. Field Data.

The sampling phase of this project involved only minor adjustments in the initial protocol. A total of 145 core, 2 soil control, 19 water, and 3 sediment samples were ultimately submitted to the laboratory for analysis. Field log information and analysis data for these samples are presented in a later section of this report.

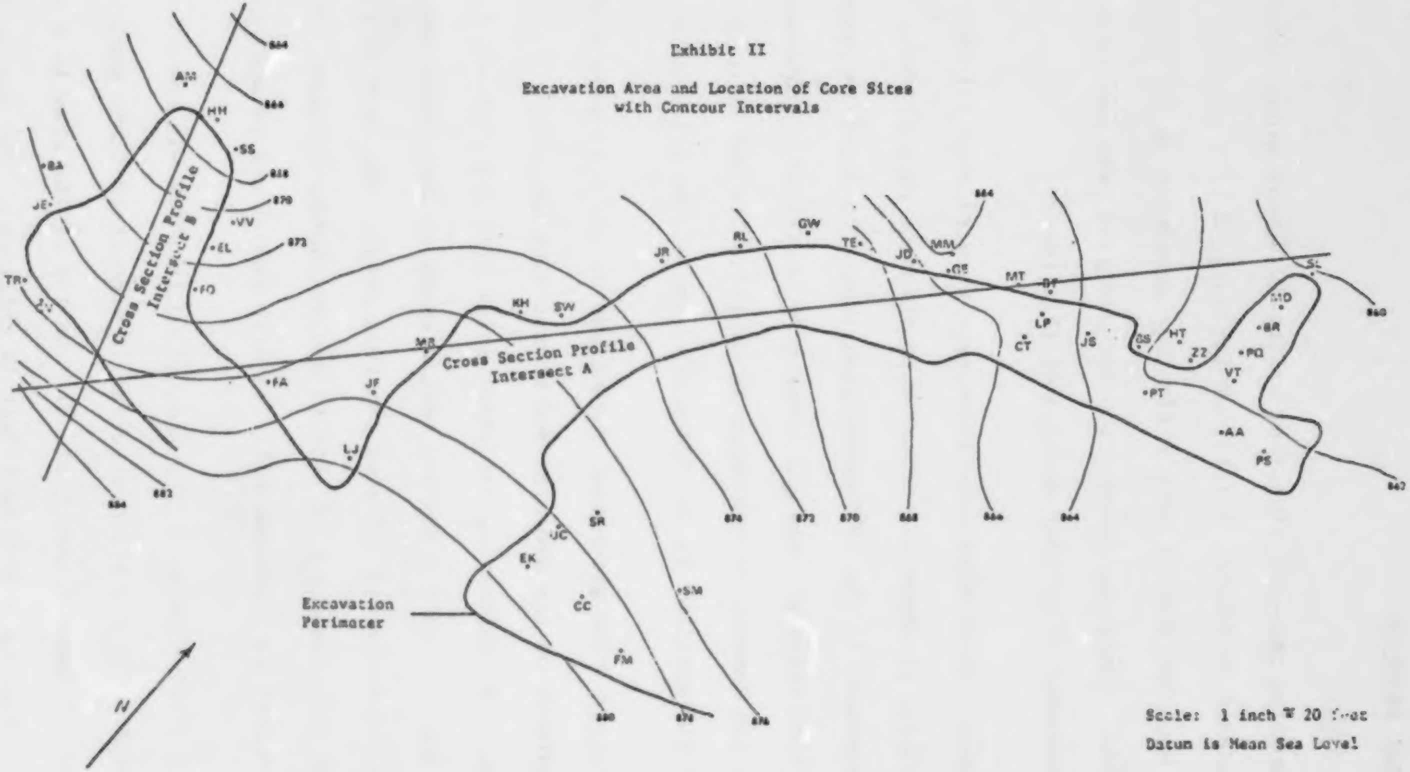
1. Cores. Forty-five core sites were sampled over a 10-day period. Exhibit II shows the relative position of each of these sites with reference to the 1973 excavation area, the local topography over a 2-foot interval, and all other core locations. Cross section profiles at two intersects are shown in Exhibits III and IV as an illustration of the gradient in the immediate area of the spill site.

2. Geology. The geological formations of the site area strike 40° northeasterly on the average, and normal dips are 25-35° to the southeast. The rocks underlying the total spill area are part of the Knox dolomite group. A shaly limestone series known as the Chickamauga formation lies to the southeast and upon the Knox group. The Knox of this area is the usual sequence of thin to massive-bedded dolomite (high $MgCO_3$ as compared to limestone with its high $CaCO_3$) and is well fractured.

   The overburden above the Knox group is thick--in the 50 to 150 foot range. The primary overburden is made up of clays mixed heavily with chert fragments (see Table 5). On top of the clay is a zone of top soil ranging from 0 to 4 feet in thickness. The top soil allows for ease of perculation while the clays are penetrable primarily through the fracture crevices of the chert.

Exhibit II

Excavation Area and Location of Core Sites with Contour Intervals


AM
HH
SS
BA
JE
VV
EL
FO
TR
ZV
Cross Section Profile Intersect B
FA
JF
LJ
MR
KH
SW
Cross Section Profile Intersect A
JR
RL
GW
TE
JD
MM
GE
MT
BF
LP
CT
JS
BS
HT
ZZ
PT
MD
BR
PQ
VT
SL
AA
PS
SR
JC
EK
CC
SM
FM
Excavation Perimeter
N
870
872
868
874
880
876

Scale: 1 inch = 20 feet
Datum is Mean Sea Level

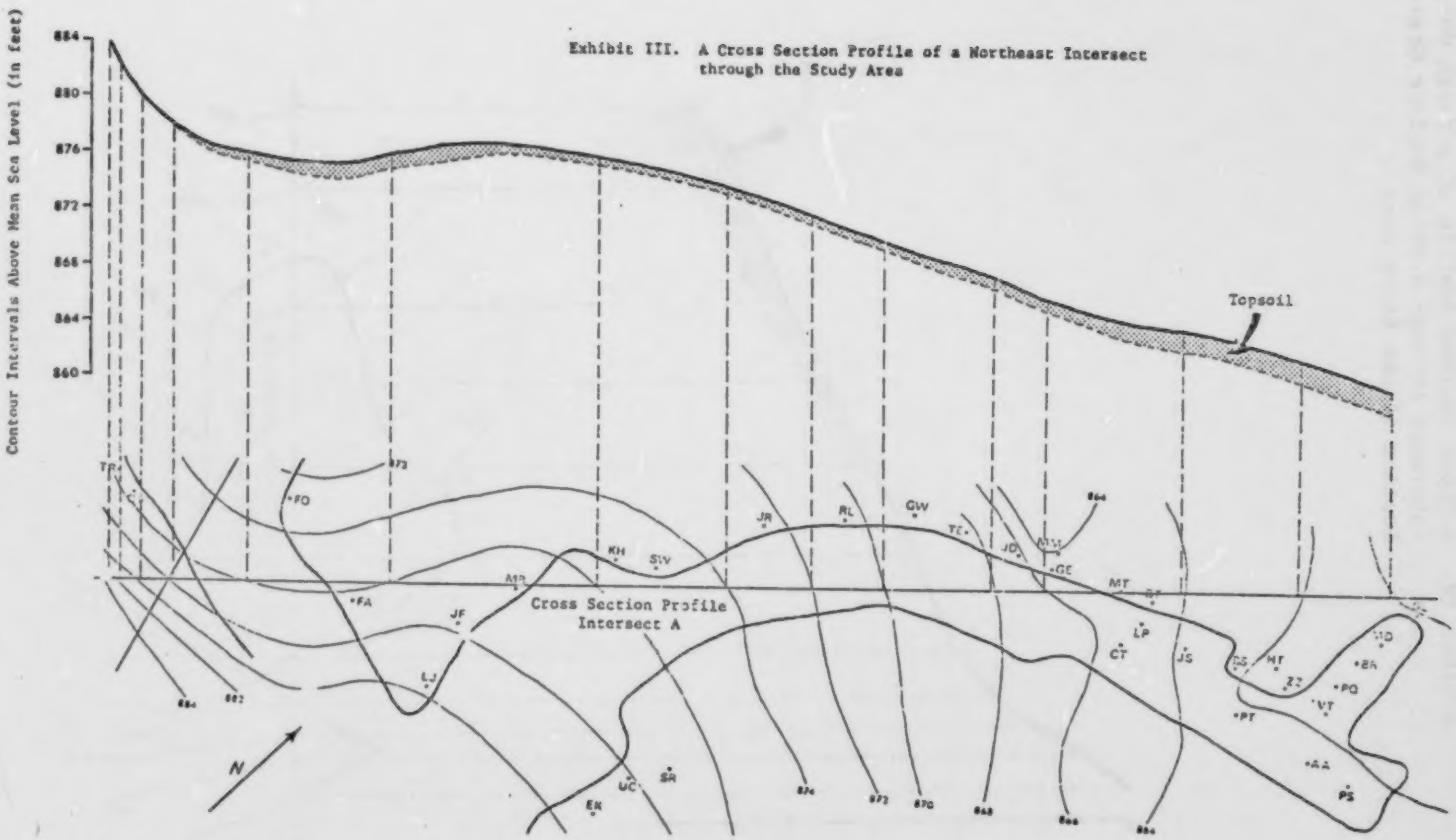
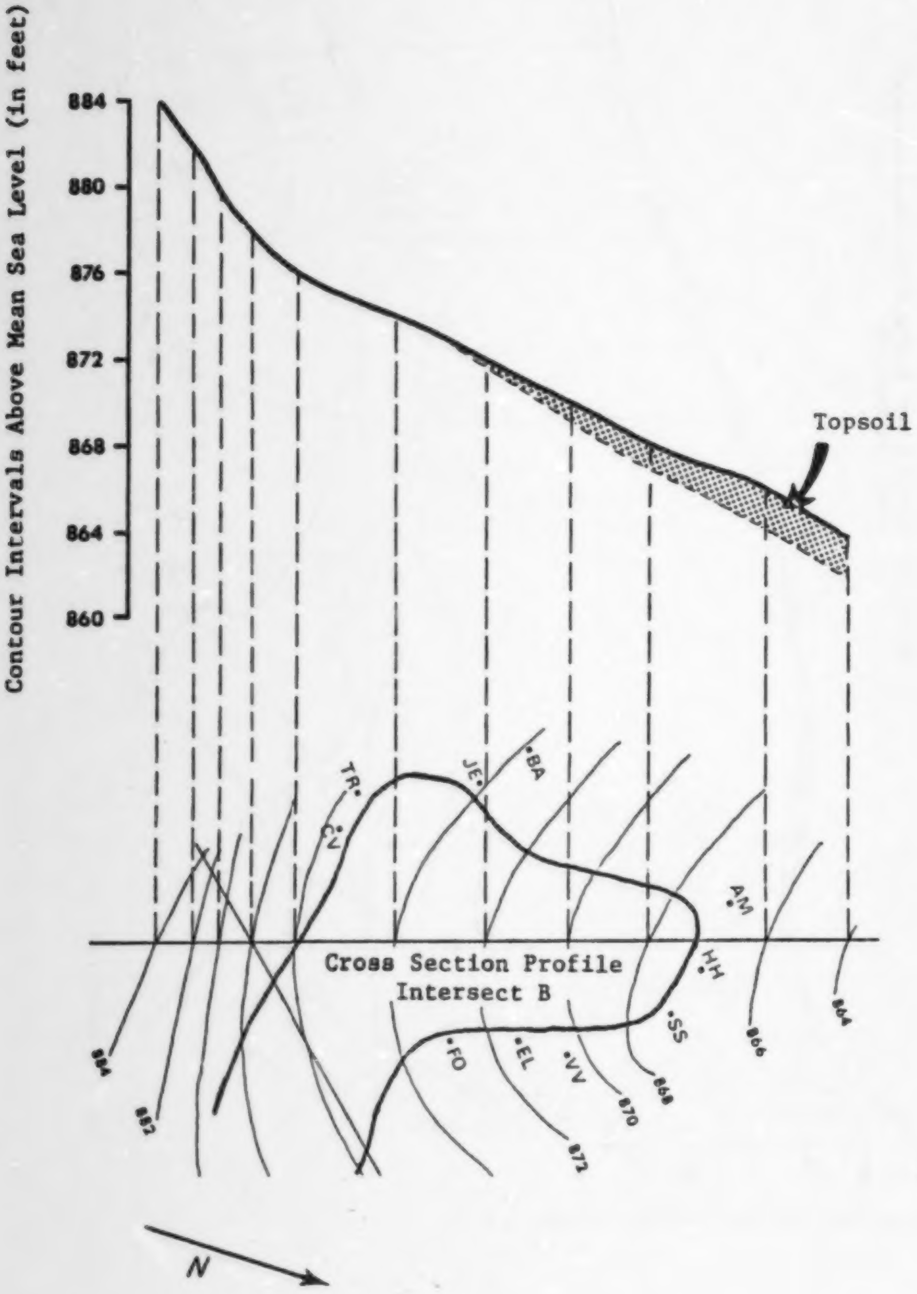

Contour Intervals Above Mean Sea Level (in feet)
884
880
876
872
868
864
860
Topsoil
TR
C
FO
872
FA
MR
JF
LJ
KH
SW
JR
RL
GW
TC
JD
MW
864
GE
MT
LP
CT
JS
DS
MT
ZZ
PT
VT
PQ
BA
VD
AA
PS
EK
UC
SA
884
882
876
872
870
868
866
864
N

Exhibit III. A Cross Section Profile of a Northeast Intersect through the Study Area

Cross Section Profile Intersect A

Scale: 1 inch=20 feet

Exhibit IV. A Cross Section Profile of a North Northwest Intersect through a Steep Surface Gradient Section of the Study Area


Contour Intervals Above Mean Sea Level (in feet)
884
880
876
872
868
864
860
Topsoil
TR.
CV
JE.
BA
AM
HH
SS
FO
EL
VV
Cross Section Profile
Intersect B
884
882
872
870
868
866
864
N

Scale: 1 inch=20 feet

Table 5. Description of Soil Types Characterizing Core Samples Taken in August 1975

Code No.	General Soil Characterizations
1	Reddish-brown clay with chert fragments
2	Yellowish-brown clay with chert fragments
3	Greyish-brown shale to reddish-brown clay
4	Reddish-brown clay
5	Greyish-brown silty clay with chert fragments
6	Greyish-brown to reddish-brown silty clay with numerous chert fragments
7	Greyish-brown to reddish-brown clay with chert fragments
8	Reddish-brown silty clay with chert fragments
9	Yellowish-brown silty clay with chert fragments
10	Greyish-brown clay with chert fragments
11	Loam (Control)

3. Environmental Samples. The spill occurred at a point where most of the drainage is geologically controlled by a northeast trending hollow near the site. This valley is aligned along the strike of the formations, and there are no visible outcrops of bedrock to indicate that sub-surface liquids would come to the surface after they entered the clay overburden.

A spring well located in the hollow seemingly provided an excellent sampling site for detecting movement of suspected spill materials in the ground water. In order to test this thesis, the spring and the mouth of the creek draining the hollow were sampled for water and sediment contamination.

Two soil control samples were taken for analytical and microbiological analyses. One site was characterized by clay and chert within the first three inches of the overburden while the clay at the other site was covered with two feet of loam.

Locations of all of these environmental sites are given in Figure 5.

4. Wells. Six wells within close proximity of the spill were chosen for analysis. These wells were included in the study because they were all located along probable geological strike formations, and 1973 data on these wells were extensive. The relative locations of the study wells are given in Figure 6.

FIGURE 5. Location of Environmental Sampling Sites

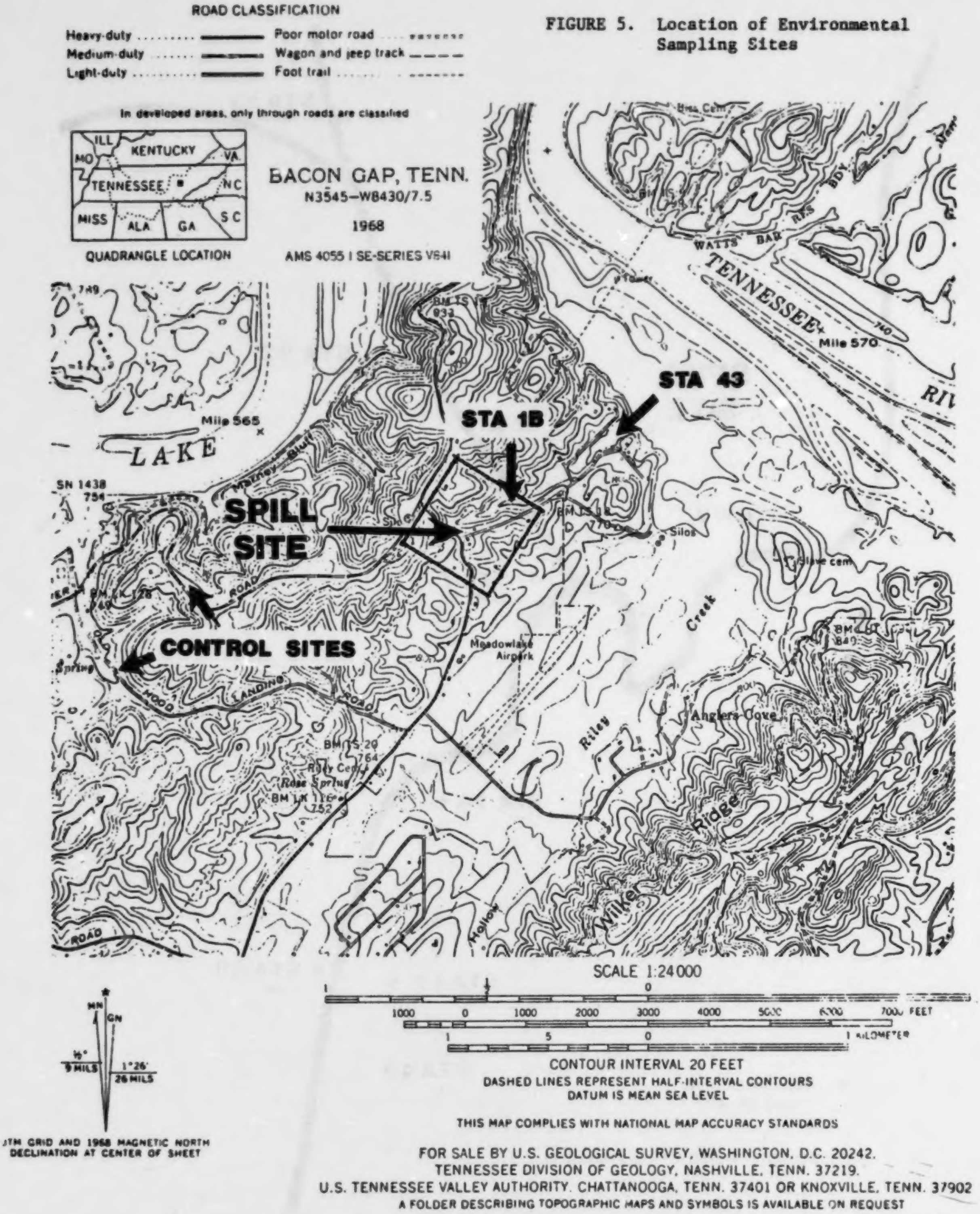
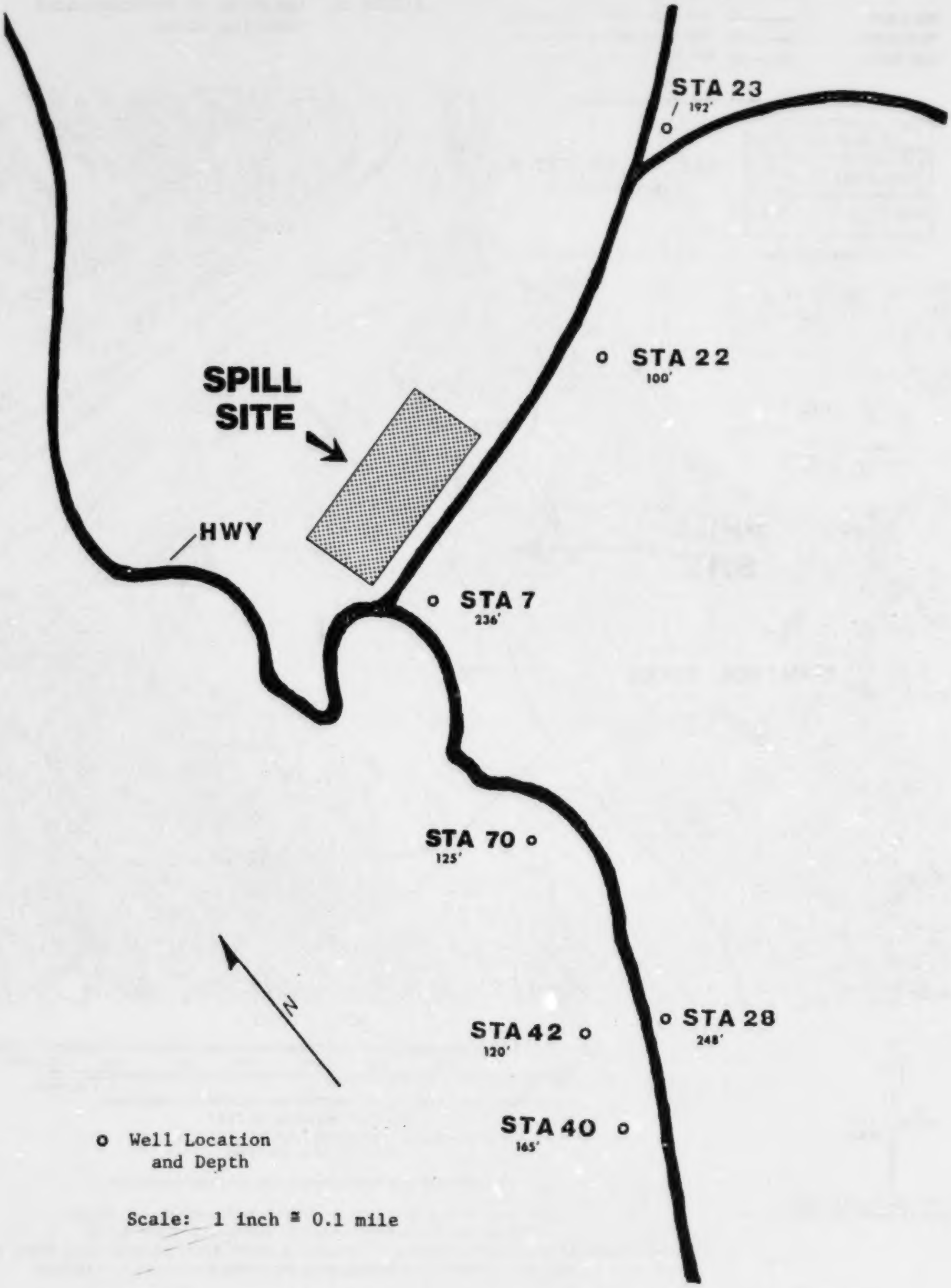

ROAD CLASSIFICATION
Heavy-duty
Medium-duty
Light-duty
Poor motor road
Wagon and jeep track
Foot trail
In developed areas, only through roads are classified
ILL
MO
KENTUCKY
VA.
TENNESSEE
NC
MISS
ALA
GA
S C
QUADRANGLE LOCATION
BACON GAP, TENN.
N3545—W8430/7.5
1968
AMS 4055 I SE-SERIES V841
STA 43
STA 1B
SPILL SITE
CONTROL SITES
TENNESSEE
RIV
WATTS BAR RES BDY
Mile 570
Mile 565
LAKE
SN 1438
754
Matney Bluff
BM LK 126
Silos
Meadowlake Airpark
Creek
Riley
Anglers Cove
Ridge
Wilkes
Hollow
BM TS 20
764
Rose Spring
BM LK 116
752
HOOD LANDING ROAD
ROAD
Spring
SCALE 1:24000
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
5
0
1 KILOMETER
CONTOUR INTERVAL 20 FEET
DASHED LINES REPRESENT HALF-INTERVAL CONTOURS
DATUM IS MEAN SEA LEVEL
THIS MAP COMPLIES WITH NATIONAL MAP ACCURACY STANDARDS
FOR SALE BY U.S. GEOLOGICAL SURVEY, WASHINGTON, D.C. 20242.
TENNESSEE DIVISION OF GEOLOGY, NASHVILLE, TENN. 37219.
U.S. TENNESSEE VALLEY AUTHORITY, CHATTANOOGA, TENN. 37401 OR KNOXVILLE, TENN. 37902
A FOLDER DESCRIBING TOPOGRAPHIC MAPS AND SYMBOLS IS AVAILABLE ON REQUEST
MN
GN
½°
9 MILS
1°26'
26 MILS
UTM GRID AND 1968 MAGNETIC NORTH DECLINATION AT CENTER OF SHEET

FIGURE 6. Locations of Well Stations Relative to the Spill Site


STA 23
192'
STA 22
100'
SPILL SITE
HWY
STA 7
236'
STA 70
125'
N
STA 42
120'
STA 28
248'
STA 40
165'
o Well Location and Depth
Scale: 1 inch ≅ 0.1 mile

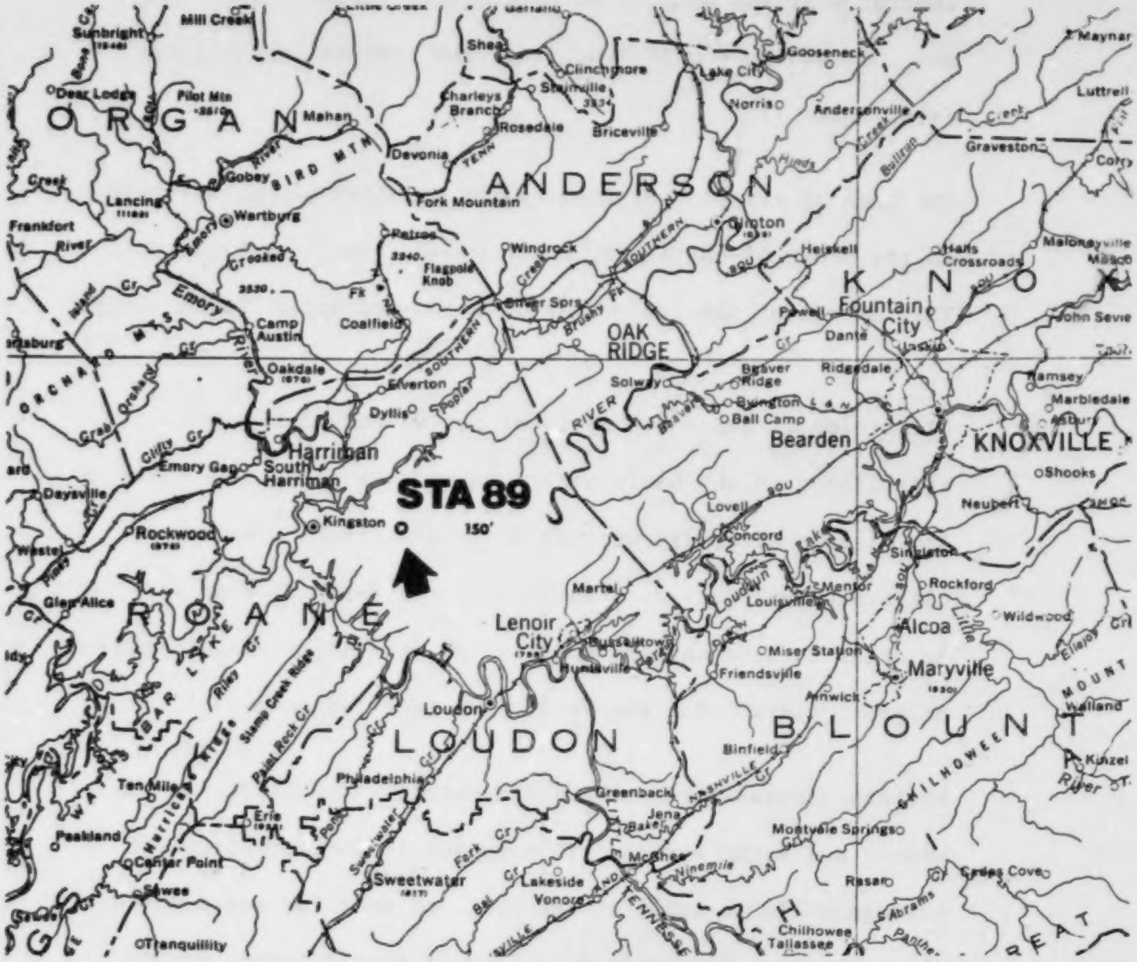
During the 1973 excavation and cleanup of the spill, a control well was sampled on numerous occasions. This well was included in the present study for comparative purposes (see Figure 7).

The time of sampling of these water supplies was predetermined in the protocol--after dry weather and after heavy rainfall. This aspect of the study will be discussed under "climatology."

5. Climatology. Since the protocol for water sampling was established on the basis of single grab samples to be taken immediately after dry weather and again after heavy rains, climatological data were obtained for a 2-1/2 year period in order to substantiate monthly, as well as, seasonal patterns of precipitation for the study area (see Table 6).

Eastern Tennessee receives its greatest rainfall during the winter and early spring. This is due to the more frequent passage of large-scale storms over and near the state during these months. A secondary maximum of precipitation occurs in mid-summer in response to shower and thunderstorm activity. This activity is especially pronounced in Eastern Tennessee where July rainfall frequently exceeds the precipitation of any other month. Normally, the lightest precipitation is observed in the fall and is brought on by the maximum occurrence of slow-moving, rain suppressing high pressure areas. Although all parts of the state are generally well supplied

FIGURE 7. Location of the Control Well


STA 89
150'
Kingston
Harriman
South Harriman
Rockwood
Oakdale
Wartburg
Lancing
Sunbright
Deer Lodge
Mill Creek
Frankfort
Coalfield
Camp Austin
Petros
Windrock
Oliver Sprs
OAK RIDGE
Solway
Clinton
Norris
Lake City
Briceville
Rosedale
Devonia
Fork Mountain
Gooseneck
Andersonville
Heiskell
Powell
Fountain City
Halls Crossroads
Graveston
Luttrell
Maynardville
KNOXVILLE
Bearden
Ball Camp
Byington
Beaver Ridge
Ridgedale
Dante
Shooks
Neubert
Marbledale
Asbury
Ramsey
Lenoir City
Loudon
Lovell
Concord
Martel
Louisville
Mentor
Singleton
Rockford
Alcoa
Maryville
Wildwood
Miser Station
Friendsville
Binfield
Greenback
Philadelphia
Sweetwater
Lakeside
Vonore
Chilhowee
Tallassee
Ten Mile
Peakland
Center Point
Tranquillity
Glen Alice
Emory Gap
Dyllis
Elverton
Montvale Springs
Kinzel
Walland
ANDERSON
KNOX
ROANE
LOUDON
BLOUNT
MORGAN
BIRD MTN
TENN
RIVER

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

STATE OF TENNESSEE

Scale 1:500,000
1 inch equals approximately 8 miles

o Well Location and Depth

Table 6. Climatological Data Showing Monthly Averages for the Study Area (1) (2)

	Total Precipitation in Inches		
Month	1973	1974	1975
January	4.51	10.00	5.93
February	3.30	5.41	5.90
March	12.44	6.97	13.19
April	4.55	3.54	2.45
May	9.82	7.36	6.43
June	7.33	2.72	4.47
July	5.81	1.64	3.63
August	3.58	5.43	2.00
September	4.32	3.10	5.17
October	3.12	1.59	5.23
November	9.74	4.26	3.87
December	8.38	7.04	4.65

(1) Climatological Data, U. S. Dept. Commerce, Annual Summary 1973, Vol. 78, No. 13, p. 2.

ibid., Annual Summary 1974, Vol. 79, No. 13, p. 2.

(2) Climatological Data, U. S. Dept. Commerce, 1975, Vol. 80, Nos. 1-9.

with precipitation; there occurs, on the average, one or more prolonged dry spells each year during the summer and fall.

Based on the foregoing information, a decision was made to obtain local daily rainfall information beginning with the inception of the project. It was apparent that over-all dry weather had prevailed from June 21 through August 27, 1975 (see Table 7). There had been minimal measurable rain (total = 5.5 in.) with three days of trace precipitation over the 68-day period; therefore, water samples were collected on August 28 and 29. During the next 29-day period, from August 29 through September 25, appreciable rain fell at the study site (total = 6.42 in.) with traces on two other days. In order to take advantage of the wet weather, the water sites were resampled on September 26.

6. Soil Temperatures. Seasonal temperature variations in the shallow layers of earth overburden are affected primarily by incoming solar radiation and outgoing terrestrial radiation. Normally, in the top two feet of surface materials there is a definite diurnal gradient which varies among various types of soils. However, daily fluctuations in soil temperature during the summer months lags considerably behind affective atmospheric temperature variations.

Differences in texture, structure, and organic matter tend to determine the moisture capacity of soils and also influence their ability to absorb and transmit heat. Rain,

Table 7. Rainfall Data Prior to and During Well Sampling

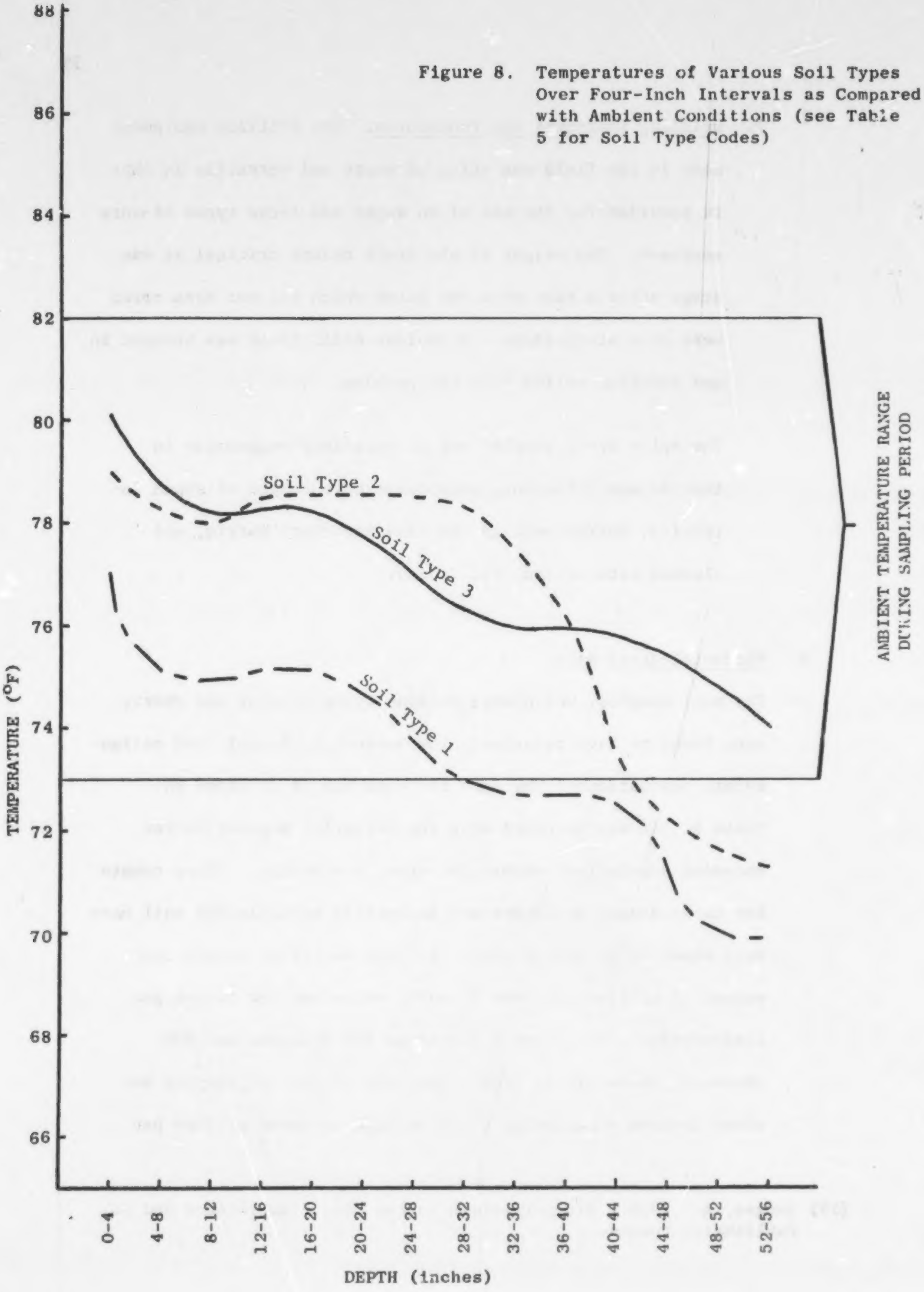
Date (1975)		Precipitation (inches)
June	21	0.02
	26	0.19
	27	0.45
	28	0.01
July	3	0.05
	6	0.24
	9	0.41
	10	Trace
	13	0.05
	16	Trace
	20	0.04
	21	0.78
	25	0.02
	26	0.10
	30	0.78
	31	0.78
August	3	0.10
	5	0.04
	6	0.56
	10	Trace
	11	0.37
	16	0.20
	19	0.12
	24	0.20
	29	0.46
September	7	0.30
	13	0.09
	17	Trace
	18	1.93
	21	0.28
	22	Trace
	23	0.98
	24	2.38

although usually at a lower temperature than the soil, generally leads to an increase in the temperature of shallow layers; however, if it falls in sufficient quantity, it can serve to increase the rate of conduction of heat from the deeper layers to the colder surface. This phenomenon can more than compensate for the initial fall of temperature due to rain.

Variations of soil types in the study area, as observed by core drillings, were minimal (see Table 5). Secondly, the over-all effect of rainfall on the area was judged to be insignificant, since climatological data indicated little rainfall prior to soil temperature measurements. On August 6, 1975, three soil types were measured for temperature gradients over four-inch intervals to a depth of fifty-six inches (see Figure 8). The ambient temperature for a 24-hour period preceding the measurements ranged from a high of 86.8°F to a low of 70°F. During the sampling period, the ambient temperature moderated to a high of 82°F with a low of 73°F.

All determinations indicated that the soil temperature was highest within the first four inches and followed a general downward trend over the remaining fifty-two inches. However, slight gradients were observed at varying depths in the three types of soil sampled. These deviations were probably due to moisture differentials caused by the non-uniform clay-chert matrix within a given sampling site.

Figure 8. Temperatures of Various Soil Types Over Four-Inch Intervals as Compared with Ambient Conditions (see Table 5 for Soil Type Codes)



7. Drilling Equipment and Procedures. The drilling equipment used in the field was quite adequate and versatile in that it provided for the use of an auger and three types of core samplers. The weight of the truck became critical at one stage after a rain when the sites which had not been cored were on a steep slope. A smaller drill truck was brought in, and provided relief from the problem.

The split spoon sampler was an excellent compromise in that it was efficient, produced a core sample of sound integrity, worked well in the clay and chert matrix, and cleaned with minimal difficulty.

B. Microbiological Data.

The soil samples, which were various types of clay and chert, were found to have relatively low bacterial, fungal, and actinomycete populations. The data for each sample is shown in Table 8. It may be noted that the bacterial population far exceeded populations within the other two groups. Plate counts for these organisms determined in fertile agricultural soil have been shown to be much higher. Average bacterial counts may exceed 15 million per gram of soil, while smaller fungal and actinomycete populations may average 400 thousand and 700 thousand, respectively (29). Only one of the 142 samples was shown to have a bacterial count as high as three million per

(29) Burges, A. 1958. Microorganisms in the Soil. Hutchinson and Co. Publishers, London.

gram, and only four others exceeded one million per gram of sample. Fungal and actinomycete counts in the samples examined were correspondingly lower than those usually found in fertile soils. Additionally, the two control soil samples, taken from areas remote to the spill, were surprisingly low for all three types of organisms.

Eleven different types of clay and chert were identified, with the majority of microorganisms occurring in types designated as 1 and 2 (see Table 9).

It may be seen that the average bacterial, fungal, and actinomycete counts for 81 samples in soil type 1 were lower than the average for all 142 samples, while populations of the three groups in soil type 2 were higher than the over-all average. Bacterial and fungal counts for soil type 2 were approximately two times as great, and actinomycete counts were greater than four times the mean for all samples. The remaining 34 samples were distributed among 8 soil types and constituted too small a group in each instance to provide statistically valid data.

Analysis of microbial populations relative to pH of the soil samples is summarized in Table 10. From these data it is obvious that conventional distribution of the three groups of organisms was observed. Bacterial and actinomycete counts were highest in samples having a pH of 5.0 to 5.9 and lowest in a pH range of 4.0-4.5. Conversely, the number of fungi were highest in the latter range and lowest at a pH of 5.0 or above.

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975.

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil		
					Bacteria	Actinomycetes	Fungi
GF 7516	19-23	2	4.6	7.30	2,310,000	2,500	25,000
GF 7520							
GF 7524			4.4	6.99.	34,500	1,500	3,500
GF 7528							
GF 7517	23-27	2	4.7	4.65	< 10,000	< 1,000	50,000
GF 7521			4.4	5.47	25,000	< 1,000	400
GF 7525			4.5	4.28	< 10,000	500	< 1,000
GF 7529							
GF 7518	27-31	2	4.5	5.65	< 10,000	< 1,000	5,000
GF 7522			4.4	2.54	< 10,000	3,000	7,200
GF 7526			4.5	3.35	25,000	5,000	32,000,000
GF 7530			4.0	10.0	< 10,000	< 1,000	< 1,000
GF /519	31-35	2	4.4	4.38	< 10,000	< 1,000	5,000
GF 7523			4.4	10.3	50,000	1,000	< 1,000
GF 7527			4.6	5.58	< 10,000	< 1,000	< 1,000
GF 7531			4.1	15.6	< 10,000	< 1,000	< 1,000
GF 7618	17-33	2	4.8	10.8	78,000	500	1,900
GF 7532	21-25	2	4.7	10.6	570,000	700	6,500
GF 7536	25-29		4.6	8.65	306,000	600	1,550
GF 7540	29-33		4.7	9.07	191,000	350	700
GF 7544	33-37		4.6	9.00	354,000	< 100	5,800

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil		
					Bacteria	Actinomycetes	Fungi
GF 7533	25-29	2	4.4	4.45	20,500	6,000	< 1,000
GF 7537			4.8	3.30	2,000,000	43,800	8,000
GF 7541			5.2	9.29	1,270,000	230,000	12,000
GF 7545			4.5	6.60	800,000	5,300	15,000
GF 7534	29-33	2	4.6	6.85	60,000	< 1,000	< 1,000
GF 7538			4.4	6.21	945,000	7,500	3,500
GF 7542			4.5	3.92	195,000	2,500	< 1,000
GF 7546			4.2	7.20	650,000	3,000	11,000
GF 7535	33-37	2	5.0	6.29	645,000	1,000	< 1,000
GF 7539			4.4	12.7	< 10,000	1,000	< 1,000
GF 7543			4.3	10.5	< 10,000	< 1,000	< 1,000
GF 7547			4.2	2.84	< 10,000	< 1,000	3,000
GF 7548	19-23	1	4.4	15.0	37,500	600	600
GF 7556			4.4	18.2	83,000	300	120
GF 7564			4.2	14.1	79,000	850	10,000
GF 7572			4.3	12.8	75,000	1,400	3,500
GF 7552	23-27	1	4.3	22.8	8,000	100	250
GF 7560			4.0	19.3	35,000	650	200
GF 7558			4.1	21.5	2,000	300	1,000
GF 7576			4.8	20.8	< 1,000	< 100	1,050
GF 7549	27-31	1	4.4	19.5	43,500	< 1,000	1,000
GF 7557			4.9	19.1	38,000	450	50
GF 7565			4.4	22.7	51,000	450	100,000
GF 7573			4.1	17.8	37,000	300	< 1,000
GF 7553	31-35	1	4.7	20.9	1,000	350	< 100
GF 7561			4.3	19.6	14,500	< 100	100
GF 7569			4.3	22.1	< 1,000	< 100	< 100
GF 7577			4.5	22.7	11,000	400	1,250

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil		
					Bacteria	Actinomycetes	Fungi
GF 7550	35-39	1	4.2	20.4	28,000	800	500
GF 7558			4.1	19.3	26,000	< 100	200
GF 7566			4.4	20.9	18,000	< 100	< 100
GF 7574			4.3	18.2	20,500	300	1,000
GF 7554	39-43	1	4.3	20.4	28,000	500	5,500
GF 7562			4.6	21.7	500	50	500
GF 7570			4.6	22.8	< 1,000	200	300
GF 7578			4.8	20.5	2,500	< 100	600
GF 7551	43-47	1	4.3	19.7	28,500	900	200
GF 7559			4.3	19.7	< 1,000	< 100	< 100
GF 7567			4.0	20.8	3,500	< 100	5,000
GF 7575			4.6	21.0	8,500	< 100	650
GF 7555	47-51	1	4.7	20.8	< 1,000	150	< 100
GF 7563			4.6	21.7	500	< 100	< 100
GF 7571			4.6	24.2	< 1,000	< 100	< 100
GF 7579			4.7	22.8	< 1,000	< 100	< 100
GF 7580	15-19	3	4.5	7.14	139,500	850	2,550
GF 7581	19-23	3	4.6	14.3	89,000	5,000	180
GF 7582	23-27	3	4.3	16.0	24,500	600	1,900
GF 7583	27-31	4	4.7	15.0	19,000	< 100	105
GF 7588	9-13	1	4.4	17.2	97,000	600	2,300
GF 7589	13-17	1	4.8	17.2	197,500	1,550	2,550
GF 7590	17-21	1	5.1	18.7	309,500	450	3,150
GF 7591	21-25	1	4.8	19.3	192,500	250	2,600
GF 7592	25-29	4	4.7	13.3	161,000	150	10,000
GF 7593	29-33	4	4.3	15.0	276,500	200	10,000
GF 7594	33-37	4	4.2	18.3	43,000	< 100	1,200
GF 7595	37-41	4	4.3	19.2	70,000	100	1,200

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil: Bacteria	Actinomycetes	Fungi
GF 7596	9-13	5	4.6	6.89	112,000	550	7,400
GF 7597	13-17	5	4.6	6.71	113,000	400	4,850
GF 7598	17-21	1	4.7	14.6	29,500	2,500	950
GF 7599	21-25	1	4.8	16.5	35,500	< 100	750
GF 7600	20-24	6	4.5	17.9	80,500	250	2,950
GF 7601	24-28	6	4.4	19.4	81,000	150	1,700
GF 7602	28-32	6	4.8	19.7	40,500	< 100	2,250
GF 7603	32-36	6	4.6	21.9	7,500	< 100	350
GF 7604	33-37	7	4.7	13.6	40,000	100	1,900
GF 7605	37-41	7	4.9	14.5	25,500	100	2,250
GF 7606	41-45	7	4.9	13.7	29,000	200	900
GF 7607	45-49	1	4.8	14.7	2,500	< 100	100
GF 7608	49-53	1	4.8	17.1	1,500	< 100	600
GF 7609	53-57	1	4.8	18.4	< 1,000	50	250
GF 7610	57-61	1	5.0	17.2	159,000	900	3,700
GF 7611	61-65	1	4.9	17.9	35,000	400	500
GF 7612	9-25	1	4.9	19.0	320,500	200	7,700
GF 7613	25-41	1	4.6	19.3	12,500	100	500
GF 7614	9-25	1	4.7	18.8	4,000	< 100	5,400
GF 7615	21-[illegible]	1	4.2	22.8	6,000	< 100	350
GF 7616	12-28	1	4.9	14.1	126,500	250	4,000
GF 7617	9-25	8	4.6	11.2	219,000	< 100	9,000
GF 7619	9-25	4	5.2	14.6	262,500	300	1,400
GF 7620	9-25	10	5.2	13.9	219,500	50	600

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches)(1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil		
					Bacteria	Actinomycetes	Fungi
GF 7621	9-25	5	5.1	13.8	215,000	250	1,800
GF 7622	9-25	5	5.6	16.0	334,000	850	350
GF 7623	25-41	5	5.5	13.9	136,000	250	1,400
GF 7624	41-57	5	5.4	14.8	46,000	200	350
GF 7625	57-73	8	4.9	23.4	2,500	< 100	50
GF 7626	19-35	5	5.5	15.3	367,000	400	13,000
GF 7627	3-19	1	5.2	24.7	4,500	< 100	100
GF 7630	9-25	5	5.3	9.00	112,500	750	2,650
GF 7631	25-41	1	5.0	7.52	157,500	50	600
GF 7632	9-25	1	5.0	9.00	218,500	650	1,900
GF 7633	25-41	1	5.2	8.40	155,000	500	1,400
GF 7634	3-19	1	4.8	25.0	100,000	< 100	200
GF 7635	4-20	1	4.6	23.5	113,500	200	1,050
GF 7636	9-25	1	5.0	12.6	82,500	450	950
GF 7637	25-41	1	4.8	22.1	29,500	250	1,100
GF 7638	3-19	1	5.2	21.2	160,000	100	750
GF 7639	9-25		5.2	22.1	60,000	250	1,500
GF 7641	25-41	1	5.3	23.6	74,500	200	1,100
GF 7640	3-19	1	5.2	22.8	48,000	< 100	5,000

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil: Bacteria	Microorganism Counts/Gram of Soil: Actinomycetes	Microorganism Counts/Gram of Soil: Fungi
GF 7642	9-25	1	5.0	19.8	315,000	400	700
GF 7643	25-41	1	5.1	18.8	96,500	1,050	4,000
GF 7644	2-9	1	5.3	21.4	204,000	200	1,350
GF 7645	9-25	1	5.3	18.5	56,500	250	1,200
GF 7646	9-25	1	5.1	20.0	57,500	700	1,650
GF 7647	25-41	1	5.8	23.3	11,000	100	800
GF 7648	9-25		5.7	16.6	1,480,000	500	2,700
GF 7649	25-41	1	5.8	15.5	170,000	350	900
GF 7650	9-25	2	5.9	13.3	665,000	20,000	3,300
GF 7651	0-16	1	4.6	23.1	500	< 100	100
GF 7652	29-45	2	5.5	7.95	65,000	150	1,400
GF 7653	21-37	2	5.8	12.9	4,500	< 100	200
GF 7654	25-37	1	4.9	10.6	17,500	200	620
GF 7655	33-45	1	5.0	11.3	138,500	400	850
GF 7656	9-2	1	4.6	21.0	4,500	< 100	< 100
GF 7657	3-19	1	4.7	12.2	291,000	250	700
GF 7658	10-26	1	4.8	11.5	3,030,000	5,500	800
GF 7659	26-42	1	4.5	13.1	165,500	100	250
GF 7660	42-58	1	4.2	20.4	1,400	< 100	50

TABLE 8. COLLECTION AND MICROBIOLOGICAL DATA FROM SOIL SAMPLES TAKEN IN AUGUST, 1975 (con't)

Field Sample Number	Sample Depth (inches) (1)	Character of Soil (2)	pH	% Moisture by Weight	Microorganism Counts/Gram of Soil		
					Bacteria	Actinomycetes	Fungi
GF 7661	9-25	10	5.2	15.6	325,000	800	2,600
GF 7662	25-41	10	5.0	18.9	26,500	100	< 100
GF 7663	9-25	5	5.0	14.1	620,000	4,000	1,700
GF 7664	25-41	5	5.0	12.8	59,500	100	350
GF 7665	3-19	5	5.0	18.9	164,000	200	550
GF 7666	9-25	5	5.3	16.5	1,540,000	450	14,500
GF 7683 (control A)	3-6	1	5.0	8.40	186,000	4,000	1,500
GF 7684 (control B)	3-6	11	6.2	3.60	340,000	11,000	1,500
		Overall Averages (3)		High	181,654	2,860	3,343
				Low	180,823	2,760	3,259

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[1] Measured from the original 1973 surface prior to backfill.

[2] See Table 5 for soil code descriptions.

[3] The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than value taken to be zero. The actual mean of the sample must lie between the high average and the low average.

Table 9. Microbial Populations Relative to Soil Types

Soil Type(1)	Criterion(2) for Average	Average Microbiological Counts (Per Gram of Soil) Bacteria	Actinomycete	Fungi	Number of Samples/Soil Type
1	High	136628	469	2707	81
	Low	136530	427	2696	
2	High	364796	12557	6093	27
	Low	360722	12183	5685	
3	High	84333	2150	1543	3
	Low	84333	2150	1543	
4	High	138667	158	3984	6
	Low	138667	125	3984	
5	High	207182	723	3127	11
	Low	207182	723	3127	
6	High	52375	150	1813	4
	Low	52375	100	1813	
7	High	31500	133	1683	3
	Low	31500	133	1683	
8	High	110750	100	4525	2
	Low	110750	0	4525	
9	High	78000	500	1900	1
	Low	78000	500	1900	
10	High	190333	317	1100	3
	Low	190333	317	1067	
11	High	340000	11000	1500	1
	Low	340000	11000	1500	

(1) See Table 5 for soil codes.

(2) The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than values taken to be zero. The actual mean of the samples must lie between the high average and the low average.

TABLE 10. Microbial Populations Relative to pH of Soil Samples

pH Ranges	Criterion[1] for Average	Average Microbiological Counts (Per Gram of Soil) Bacteria	Actinomycete	Fungi	Number of Samples
4.0-4.5	High	90324	1043	4444	49
	Low	88447	861	4275	
4.6-5.0	High	215644	1299	2901	66
	Low	215250	1225	2845	
5.0 Up	High	264315	9970	2426	27
	Low	264315	9959	2426	

(1) The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than values taken to be zero. The actual mean of the samples must lie between the high average and the low average.

It is well recognized that fungi thrive best in a relatively acid environment while bacteria and actinomycetes, in general, prefer a more neutral pH range for survival and growth.

Microbial counts were compared in relation to moisture content of the soil samples. Determinations were made in the ranges of 0-5, 5-10, 10-15, 15-20, 20-25, and 25-30 percent moisture by weight. From Table 11 it can be observed that the highest bacterial and actinomycete concentrations were present in samples having 5-10 percent moisture. Fungal counts were the greatest in samples having the least moisture. A single sample having a 25-30 percent moisture was insufficient to provide valid data at that level. In fertile soils, rich in nutrients, it might be expected that extremely high numbers of organisms would be detected when moisture levels were high since water is required to solubilize the nutrients, making them more readily available to the soil populations. However, in clay and chert where nutrients are extremely deficient, and where the pH range is predominately between 4.0 and 5.0, soluble acid minerals contributing to the low pH may function bacteriostatically or bactericidally to maintain relatively low levels of organisms. Very significant decreases in bacterial counts were observed when moisture content of the samples exceeded 20 percent, and for actinomycetes when moisture was above 10 percent. Fungal populations decreased steadily as moisture content increased to 20 percent. Above this level a slight increase in fungi was noted between 20-25 percent moisture.

Table 11. Microbial Populations Relative to Moisture Content of Soils

Moisture (% by Weight)	Criterion[(1)] for Average	Average Microbiological Counts (Per Gram of Soil)			Number of Samples
		Bacteria	Actinomycete	Fungi	
0%- 5%	High	289500	7756	8633	9
	Low	289500	7756	8633	
5%-10%	High	385630	11476	4813	23
	Low	385630	11476	4813	
10%-15%	High	236156	1503	2202	32
	Low	236156	1503	2202	
15%-20%	High	135940	407	1976	42
	Low	135940	407	1976	
20%-25%	High	27240	200	3791	35
	Low	27240	200	3791	
25%-30%	High	100000	100	200	1
	Low	100000	100	200	

(1) The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than values taken to be zero. The actual mean of the samples must lie between the high average and the low average.

It has been reported (30, 31, 32) that microbial counts in fertile agricultural soil are the highest in the first 6-8 inches below the surface, decreasing rapidly below that point to only a few hundred per gram at depths of 6 feet or more. Although these data were obtained from samples deficient in nutrients at any depth, a similar trend could be observed. The major difference was revealed in Table 12 by bacterial counts which averaged 157,330 per gram between 0 and 8 inches and increased to 271,700 per gram between 8 and 29 inches. Below 29 inches the bacterial population was reduced progressively to a total of 2500 per gram in a single sample taken at a depth below 66 inches. Actinomycete counts were highest between 0 and 2 inches and at a depth of 24-29 inches, subsequently decreasing to 100-700 per gram at all depths below 29 inches. Fungal counts were highest between 8 and 27 inches, and these also decreased progressively below that level except for a very slight increase in numbers in 13 samples taken at a depth between 56 and 61 inches.

The fact that bacterial counts near the surface of the soil were slightly lower than at depths of 8-29 inches may possibly be attributed to the seasonal effect of high summer temperatures which would tend to kill some of the organisms by baking of the soil to shallow depths.

(30) Waksman, S. A., and Starkey, R. L. 1931. Soil and the Microbe. Wiley and Sons, Inc., Publishers, New York.

(31) Kuster, E. and Williams S. T. 1964. Selections of Media for Isolation of Streptomycetes. Nature, London, 202:928-929.

(32) Frobisher, M. 1962. Fundamentals of Microbiology (p. 652). W. B. Saunders Co. Publishers, Philadelphia, Pennsylvania.

TABLE 12. Microbial Populations Relative to Core Sample Depths

Depth below Surface (inches)	Criterion for Average (1)	Average Microbiological Counts (Per Gram of Soil)			Number of Samples/Depth Category
		Bacteria	Actinomycete	Fungi	
0	High	175500	5033	1033	3
	Low	175500	5000	1033	
1	High	175500	5033	1033	3
	Low	175500	5000	1033	
2	High	182625	3825	1113	4
	Low	182625	3800	1113	
3	High	149800	1615	1175	10
	Low	149800	1575	1175	
4	High	146500	1486	1164	11
	Low	146500	1450	1164	
5	High	146500	1486	1164	11
	Low	146500	1450	1164	
6	High	146500	1486	1164	11
	Low	146500	1450	1164	
7	High	146500	1486	1164	11
	Low	146500	1450	1164	
8	High	146500	1486	1164	11
	Low	146500	1450	1164	
9	High	211554	1392	2538	37
	Low	211554	1373	2536	
10	High	287932	1535	2524	37
	Low	287932	1516	2521	
11	High	289357	1194	2582	35
	Low	289357	1174	2579	
12	High	284833	1168	2621	36
	Low	284833	1149	2619	
13	High	256058	1079	4973	43
	Low	256058	1040	4970	

TABLE 12. Microbial Populations Relative to Core Sample Depths (Continued)

Depth below Surface (inches)	Criterion$^{(1)}$ for Average	Average Microbiological Counts (Per Gram of Soil)			Number of Samples/Depth Category
		Bacteria	Actinomycete	Fungi	
14	High	287944	1165	4997	36
	Low	287944	1118	4994	
15	High	283932	1157	4931	37
	Low	283932	1111	4928	
16	High	283932	1157	4931	37
	Low	283932	1111	4928	
17	High	251307	1081	4349	44
	Low	251307	1038	4344	
18	High	278405	1168	1943	37
	Low	278405	1143	1938	
19	High	319549	1283	2770	41
	Low	319549	1261	2765	
20	High	350714	1461	3048	35
	Low	350714	1444	3042	
21	High	297307	1216	2800	44
	Low	297284	1189	2793	
22	High	340730	1328	3137	37
	Low	340703	1304	3132	
23	High	309183	1274	4131	41
	Low	308671	1204	4102	
24	High	264718	1113	3651	39
	Low	264179	1038	3621	
25	High	266586	5743	3301	58
	Low	266207	5691	3262	
26	High	285828	9380	3985	32
	Low	285172	9308	3919	
27	High	176157	8564	4001	35
	Low	174700	8439	3912	
28	High	191766	9273	2780	32
	Low	190797	9195	2715	

TABLE 12. Microbial Populations Relative to Core Sample Depths (Continued)

Depth below Surface (inches)	Criterion(1) for Average	Average Microbiological Counts (Per Gram of Soil)			Number of Samples/Depth Category
		Bacteria	Actinomycete	Fungi	
29	High	201563	7795	2586	40
	Low	200763	7703	2478	
30	High	116774	798	2044	31
	Low	115774	682	1938	
31	High	105714	821	2039	35
	Low	103971	633	1859	
32	High	114328	742	1826	32
	Low	113359	598	1660	
33	High	116919	685	1826	43
	Low	115477	529	1633	
34	High	87303	414	1754	33
	Low	85455	247	1569	
35	High	87303	414	1754	33
	Low	85455	247	1569	
36	High	86929	330	1317	28
	Low	85821	241	1206	
37	High	76734	303	1224	32
	Low	75672	219	1115	
38	High	69816	224	916	19
	Low	69658	208	889	
39	High	69816	224	916	19
	Low	69658	208	889	
40	High	69816	224	916	19
	Low	69658	208	889	
41	High	66738	221	888	21
	Low	66595	207	864	

TABLE 12. Microbial Populations Relative to Core Sample Depths (Continued)

Depth below Surface (inches)	Criterion(1) for Average	Average Microbiological Counts (Per Gram of Soil)			Number of Samples/Depth Category
		Bacteria	Actinomycete	Fungi	
42	High	87914	214	671	7
	Low	87914	200	671	
43	High	74983	233	742	6
	Low	74983	217	742	
44	High	74983	233	742	6
	Low	74983	217	742	
45	High	64629	214	650	7
	Low	64629	186	650	
46	High	54975	188	350	4
	Low	54975	138	350	
47	High	54975	188	350	4
	Low	54975	138	350	
48	High	54975	188	350	4
	Low	54975	138	350	
49	High	44280	170	400	5
	Low	44280	110	400	
50	High	16300	133	333	3
	Low	16300	67	333	
51	High	16300	133	333	3
	Low	16300	67	333	
52	High	16300	133	333	3
	Low	16300	67	333	
53	High	12475	113	313	4
	Low	12225	63	313	
54	High	16133	117	217	3
	Low	15800	83	217	
55	High	16133	117	217	3
	Low	15800	83	217	

TABLE 12. Microbial Populations Relative to Core Sample Depths (Continued)

Depth below Surface (inches)	Criterion(1) for Average	Average Microbiological Counts (Per Gram of Soil) Bacteria	Actinomycete	Fungi	Number of Samples/Depth Category
56	High	16133	117	217	3
	Low	15800	83	217	
57	High	41980	270	880	5
	Low	41780	230	880	
58	High	54300	367	1267	3
	Low	54300	300	1267	
59	High	80750	500	1875	2
	Low	80750	450	1875	
60	High	80750	500	1875	2
	Low	80750	450	1875	
61	High	65500	467	1417	3
	Low	65500	433	1417	
62	High	18750	250	275	2
	Low	18750	200	275	
63	High	18750	250	275	2
	Low	18750	200	275	
64	High	18750	250	275	2
	Low	18750	200	275	
65	High	18750	250	275	2
	Low	18750	200	275	
66	High	2500	100	50	1
	Low	2500	0	50	
67	High	2500	100	50	1
	Low	2500	0	50	
68	High	2500	100	50	1
	Low	2500	0	50	

TABLE 12. Microbial Populations Relative to Core Samplc Depths (Continued)

Depth below Surface (inches)	Criterion(1) for Average	Average Microbiological Counts (Per Gram of Soil) Bacteria	Actinomycete	Fungi	Number of Samples/Depth Category
69	High	2500	100	50	1
	Low	2500	0	50	
70	High	2500	100	50	1
	Low	2500	0	50	
71	High	2500	100	50	1
	Low	2500	0	50	
72	High	2500	100	50	1
	Low	2500	0	50	
73	High	2500	100	50	1
	Low	2500	0	50	

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(1) The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than values taken to be zero. The actual mean of the samples must lie between the high average and the low average.

Analysis of microbial populations exposed to polychlorinated biphenyl (PCB) in the soil suggested a possible stimulating effect of this compound in concentrations between 0.05 and 5.0 mg/kg on both the bacteria and actinomycetes, as shown in Table 13. The lowest bacterial counts were obtained in samples where PCB levels were less than 0.05 mg/kg. Although only three samples were contaminated with PCB in excess of 10 mg/kg, the bacterial counts were greater than in relatively uncontaminated soil having less than 0.05 mg/kg. Fungal counts were essentially unaffected in all except the one sample having the highest concentration of PCB.

In summary, the relatively low microbial counts are compatible with the clay and chert soils which are largely devoid of nutrients. The soil acidity is also reflected by the low bacterial counts. Excessive moisture did not appear to influence an increase in the microbial populations of the soil; and, in fact, the lowest bacterial and actinomycete counts were observed in samples having a moisture content of 20-25 percent while the highest numbers were found in samples having 0.5-10.0 percent moisture.

The most interesting observation was the correlation between microorganism counts and the soil samples containing 0.05-5.0 mg/kg of the polychlorinated biphenyl compounds. Bacterial counts in 55 samples were shown to be 50 percent higher than the mean for all samples, and actinomycete counts were similarly 100 percent greater.

TABLE 13. Microbial Populations Relative to PCB Concentration in Core Samples

PCB Concentration (mg/kg soil)	Criterion[1] for Average	Average Microbiological Counts (Per Gram of Soil)			Number of Samples
		Bacteria	Actinomycete	Fungi	
<.05	High	82825	1066	3378	80
	Low	81475	936	3242	
.05-5.0	High	273535	5708	3269	55
	Low	273353	5643	3249	
5.0-10.0	High	920750	1500	4638	4
	Low	920750	1475	4638	
10.0-30.0	High	140750	375	2700	2
	Low	140750	375	2700	
30.0-66.6	High	160000	100	750	1
	Low	160000	100	750	

(1) The high averages are calculated with less than values taken to be positive (<.1 taken as .1). The low averages are calculated with the less than values taken to be zero. The actual mean of the samples must lie between the high average and the low average.

C. Analytical Data From Electron-Capture Gas Chromatography (EC/GC).

During Phase Two of this project, a total of 145 core, three sediment, and two control soil samples were analyzed quantitatively for Aroclor 1254. Analytical and collection data for soils are contained in three tables. Data for the three test core sites are in Table 14, data for the five core sites sampled at four-inch intervals are in Table 15, and the remainder of the core samples are in Table 16. The nineteen water samples collected for this project were analyzed for both Aroclor 1254 and the askarel solvent. Results for these analyses plus those for sediment and control soils are given in Table 17. No analysis difficulties were encountered during the course of this project.

D. Special Soil Extraction Experiment.

In 1973, data relating to the concentration of PCBs in soil and sediment were obtained using hexane as the solvent for the extraction. Two other extraction systems were recommended for consideration by the project officer for Contract No. 68-01-3232. The first employs a dual hexane/acetone system (33), and the second extracts with 15% methylene chloride in hexane (V/V) (34). Eight of the larger samples were selected for comparative analysis using the three extraction systems. In two instances, there was

(33) Crump-Wiesner, H. J., Feltz, H. R., and Yates, M. D., 1973, A Study of the distribution of polychlorinated biphenyls in the aquatic environment: Jour. Research U. S. Geol. Survey, v. 1, no. 5, p. 603-607.

(34) National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II (11-28-73).

TABLE 14. Collection and Analytical Data From Three Test Core Sites Sampled Over Four-Inch Intervals in August 1975

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
RL-1	GF7516	19-23	2	1.51
RL-2	GF7520			0.95
RL-3	GF7524			1.52
RL-4	GF7528			14.5
RL-1	GF7517	23-27	2	<0.05
RL-2	GF7521			<0.05
RL-3	GF7525			<0.05
RL-4	GF7529			10.9
RL-1	GF7518	27-31	2	<0.05
RL-2	GF7522			<0.05
RL-3	GF7526			<0.05
RL-4	GF7530			0.18
RL-1	GF7519	31-35	2	<0.05
RL-2	GF7523			<0.05
RL-3	GF7527			<0.05
RL-4	GF7531			<0.05
RL-5	GF7618	17-33	2	0.16

[1] See Exhibit IIfor general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

TABLE 14. Collection and Analytical Data From Three Test Core Sites Sampled Over Four-Inch Intervals in August 1975 (Continued)

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
UC-1	GF7532	21-25	2	0.09
UC-2	GF7536			<0.05
UC-3	GF7540			<0.05
UC-4	GF7544			0.16
UC-1	GF7533	25-29	2	<0.05
UC-2	GF7537			0.70
UC-3	GF7541			0.16
UC-4	GF7545			2.24
UC-1	GF7534	29-33	2	<0.05
UC-2	GF7538			0.52
UC-3	GF7542			<0.05
UC-4	GF7546			<0.05
UC-1	GF7535	33-37	2	<0.05
UC-2	GF7539			<0.05
UC-3	GF7543			<0.05
UC-4	GF7547			<0.05

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[1] See Exhibit II for general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

TABLE 14. Collection and Analytical Data From Three Test Core Sites Sampled Over Four-Inch Intervals in August 1975 (Continued)

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
JF-1	GF7548	19-23	1	0.36
JF-2	GF7556			<0.05
JF-3	GF7564			0.08
JF-4	GF7572			0.17
JF-5	GF7552	23-27	1	<0.05
JF-6	GF7560			<0.05
JF-7	GF7568			<0.05
JF-8	GF7576			<0.05
JF-1	GF7549	27-31	1	0.27
JF-2	GF7557			<0.05
JF-3	GF7565			<0.05
JF-4	GF7573			<0.05
JF-5	GF7553	31-35	1	<0.05
JF-6	GF7561			<0.05
JF-7	GF7569			<0.05
JF-8	GF7577			<0.05
JF-1	GF7550	35-39	1	<0.05
JF-2	GF7558			<0.05
JF-3	GF7566			<0.05
JF-4	GF7574			<0.05
JF-5	GF7554	39-43	1	<0.05
JF-6	GF7562			<0.05
JF-7	GF7570			<0.05
JF-8	GF7578			0.18
JF-1	GF7551	43-47	1	<0.05
JF-2	GF7559			<0.05
JF-3	GF7567			0.25
JF-4	GF7575			0.24
JF-5	GF7555	47-51	1	<0.05
JF-6	GF7563			<0.05
JF-7	GF7571			<0.05
JF-8	GF7579			<0.05

[1] See Exhibit II for general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

TABLE 15. Collection and Analytical Data From Core Sites Sampled Over Four-Inch Intervals in August 1975

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
EK-1	GF7580	15-19	3	0.13
EK-2	GF7581	19-23	3	<0.05
EK-3	GF7582	23-27	3	0.27
EK-4	GF7583	27-31	4	0.13
SR-1	GF7888	9-13	1	0.08
SR-2	GF7589	13-17	1	0.24
SR-3	GF7590	17-21	1	0.89
SR-4	GF7591	21-25	1	<0.05
SR-5	GF7592	25-29	4	<0.05
SR-6	GF7593	29-33	4	<0.05
SR-7	GF7594	33-37	4	<0.05
SR-8	GF7595	37-41	4	<0.05
CC-1	GF7596	9-13	5	0.17
CC-2	GF7597	13-17	5	0.40
CC-3	GF7598	17-21	1	<0.05
CC-4	GF7599	21-25	1	0.14
SM-1	GF7600	20-24	6	<0.05
SM-2	GF7601	24-28	6	0.08
SM-3	GF7602	28-32	6	1.10
SM-4	GF7603	32-36	6	0.11
FM-1	GF7604	33-37	7	0.22
FM-2	GF7605	37-41	7	<0.05
FM-3	GF7606	41-45	7	0.14
FM-4	GF7607	45-49	1	0.09
FM-5	GF7608	49-53	1	<0.05
FM-6	GF7609	53-57	1	<0.05
FM-7	GF7610	57-61	1	1.27
FM-8	GF7611	61-65	1	1.21

[1] See Exhibit II for general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

TABLE 16. Collection and Analytical Data from Core Sites Sampled Over Sixteen-Inch Intervals in August 1975

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
LJ-1-4	GF7612	9-25	1	7.36
LJ-5-8	GF7613	25-41	1	<0.05
MB-1-4	GF7614	9-25	1	3.69
KH-1-4	GF7615	21-37	1	<0.05
SW-1-4	GF7616	12-28	1	23.8
JR-1-4	GF7617	9-25	8	5.00
GW-1-4	GF7619	9-25	4	3.23
TE-1-4	GF7620	9-25	10	<0.05
JD-1-4	GF7621	9-25	5	0.17
MM-1-4	GF7622	9-25	5	0.27
MM-5-8	GF7623	25-41	5	<0.05
MM-9-12	GF7624	41-57	5	<0.05
MM-13-16	GF7625	57-73	8	<0.05
GE-1-4	GF7626	19-35	5	0.32
CT-1-4	GF7627	3-19	1	0.16
MT-1-4	GF7630	9-25	5	4.35
MT-5-8	GF7631	25-41	1	0.89
BT-1-4	GF7632	9-25	1	1.34
BT-5-8	GF7633	25-41	1	10.1
LP-1-4	GF7634	3-19	1	3.41
JS-1-4	GF7635	4-20	1	5.62
FA-1-4	GF7636	9-25	1	<0.05
FA-5-8	GF7637	25-41	1	<0.05

[1] See Exhibit II for general location
[2] Measured from the original 1973 surface prior to backfill
[3] See Table 5 for soil code descriptions

TABLE 16. Collection and Analytical Data from Core Sites Sampled Over Sixteen-Inch Intervals in August 1975 (Continued)

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
PT-1-4	GF7638	3-19	1	66.6
FO-1-4	GF7639	9-25		<0.05
FO-5-8	GF7641	25-41	1	<0.05
AA-1-4	GF7640	3-19		0.34
EL-1-4	GF7642	9-25	1	<0.05
EL-5-8	GF7643	25-41	1	<0.05
PS-1-4	GF7644	2-9	1	2.04
VV-1-4	GF7645	9-25	1	<0.05
SS-1-4	GF7646	9-25	1	<0.05
SS-5-8	GF7647	25-41	1	<0.05
HH-1-4	GF7648	9-25		0.67
HH-5-8	GF7649	25-41	1	0.12
AM-1-4	GF7650	9-25	2	<0.05
VT-1-4	GF7651	0-16	1	0.17
JE-1-4	GF7652	29-45	2	<0.05
BA-1-4	GF7653	21-37	2	<0.05
TR-1-4	GF7654	25-37	1	<0.05
CV-1-4	GF7655	33-45	1	<0.05
PQ-1-4	GF7656	9-25	1	0.21
MD-1-4	GF7657	3-19	1	0.15
BS-1-4	GF7658	10-26	1	7.45
BS-5-8	GF7659	26-42	1	0.26
BS-9-12	GF7660	42-58	1	0.13

[1] See Exhibit II for general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

TABLE 16. Collection and Analytical Data from Core Sites Sampled Over Sixteen-Inch Intervals in August 1975 (Continued)

Core Site Identification[1]	Field Sample Number	Sample Depth[2] (Inches)	Character[3] of Soil	PCB Concentration (mg/kg)
HT-1-4	GF7661	9-25	10	0.16
HT-5-8	GF7662	25-41	10	<0.05
ZZ-1-4	GF7663	9-25	5	0.29
ZZ-5-8	GF7664	25-41	5	0.50
BR-1-4	GF7665	3-19	5	0.91
SL-1-4	GF7666	9-25	5	2.05

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[1] See Exhibit II for general location

[2] Measured from the original 1973 surface prior to backfill

[3] See Table 5 for soil code descriptions

Table 17. Aroclor 1254 and Askarel Solvent Analyses for Water, Sediment, and Control Soil Samples

WATER

Concentrations are expressed as µg/liter (ppb)

Date Collected	Field Location	Sample Number	Aroclor 1254	Total Solvent	1,2,4-trichloro-benzene	1,2,3-trichloro-benzene	1,2,4,5-tetrachloro-benzene	1,2,3,4-tetrachloro-benzene	penta-chloro-benzene
8-28-75	Sta. 7	PP 2257	<0.5	1.23	-	0.18	0.47	0.33	0.25
8-29-75	Sta. 1B	PP 2258	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 22	PP 2260	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 43	PP 2261	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 23	PP 2263	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 28	PP 2264	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 42	PP 2265	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 40	PP 2266	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 70	PP 2267	<0.5	<0.006	-	-	-	-	-
8-29-75	Sta. 89	PP 2268	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 43	PP 2270	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 23	PP 2271	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 22	PP 2272	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 40	PP 2273	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 42	PP 2274	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 28	PP 2275	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 70	PP 2276	<0.5	<0.006	-	-	-	-	-
9-26-75	Sta. 7	PP 2277	<0.5	0.92	0.006	0.097	0.417	0.152	0.245
9-26-75	Sta. 89	PP 2278	<0.5	<0.006					
	Sta. 1B		Collection Permission Refused						

SEDIMENT AND CONTROL SOILS

Concentrations are expressed as mg/kg (dry basis)

Date Collected	Field Location	Sample Number	Aroclor 1254	Total Solvent	1,2,4-trichloro-benzene	1,2,3-trichloro-benzene	1,2,4,5-tetrachloro-benzene	1,2,3,4-tetrachloro-benzene	penta-chloro-benzene
8-29-75	Sta. 1B	PP 2259	<0.05	0.016	-	-	-	0.016	-
8-29-75	Sta. 43	PP 2262	<0.05	<0.010	-	-	-	-	-
9-26-75	Sta. 43	PP 2269	<0.05	<0.010	-	-	-	-	-
8-14-75	Control A	GF 7683	<0.05						
8-14-75	Control B	GF 7684	<0.05						

insufficient sample available for triplicate determinations. Comparative data are found in Table 18. Based on this experiment, all three solvent systems are equally effective in the extraction of PCBs from the clay soil present at the spill site. Round-robin studies in 1973, including the contractor and the control agencies involved with the askarel spill, showed similar correlation between the use of hexane only as the extractant when compared to a dual hexane/acetone solvent system.

E. Quality Assurance Data.

The quality assurance for this project was provided by an in-house quality control program. Duplicate blind sample splits for use as quality control checks were prepared as soon as the air-dried samples were screened; therefore, the quality control data are representative of both method and sample reproducibility. Results of these analyses are tabulated in Table 19.

The eight samples involved in the special solvent extraction experiment were also included in the in-house quality control program. In order to more accurately assess the precision of the data, the results from these two sources were combined; and an average percent coefficient of variation was determined for the samples involved. Tabulation of the data is found in Table 20. The average coefficient of variation based on these results is ± 6.6%.

Table 18. Results from Special Soil Extraction Experiment --Aroclor 1254

Concentrations are expressed as mg/kg (dry-weight basis)

Sample Identification	Solvent System Hexane	Hexane/Acetone	Hexane-15% Methylene Chloride
GF 7616	20.7	20.7	22.0
GF 7617	7.24	5.46	5.94
GF 7635	5.36	6.12	5.19
GF 7640	0.31	0.35	0.43
GF 7644	2.08	2.22	*
GF 7648	0.82	0.74	0.73
GF 7654	<0.05	<0.05	<0.05
GF 7675	4.35	3.50	*

*Insufficient sample for experiment

TABLE 19. In-house Quality Control Data--Aroclor 1254

Concentrations are expressed as mg/kg (dry basis)

Sample Code	Original Analysis	Duplicate Analysis
GF 7545	2.24	1.64
GF 7589	0.24	0.34
GF 7608	<0.05	<0.05
GF 7609	<0.05	<0.05
GF 7610	1.27	1.22
GF 7611	1.21	1.21
GF 7616	23.8	18.0
GF 7617	5.00	5.65
GF 7627	0.16	0.06
GF 7635	5.62	5.39
GF 7640	0.34	0.31
GF 7644	2.04	2.08
GF 7648	0.67	0.82
GF 7654	<0.05	<0.05
GF 7675	4.35	5.44

Table 20. Percent Coefficient of Variation Evaluation for In-house Quality Control Data--Aroclor 1254

Concentrations are expressed as mg/kg dry basis

Sample Code	Average Value	Original Analysis	QC Blind Split	Hexane Solvent	Hexane/ Acetone	Hexane Methylene Chloride	Average C.O.V. (%)
GF 7616	21.0	23.8	18.0	20.7	20.7	22.0	
% C.O.V.		±13.	±14.	±1.4	±1.4	±4.8	±6.9
GF 7617	5.86	5.00	5.65	7.24	5.46	5.94	
% C.O.V.		±15.	±3.6	±24.	±6.8	±1.4	±10.2
GF 7635	5.54	5.62	5.39	5.36	6.12	5.19	
% C.O.V.		±1.4	±2.7	±3.2	±10.	±6.3	±4.7
GF 7640	0.35	0.34	0.31	0.31	0.35	0.43	
% C.O.V.		±2.9	±11.	±11.	±0.	±23.	±9.6
GF 7644	2.11	2.04	2.08	2.08	2.22	-	
% C.O.V.		±3.3	±1.4	±1.4	±5.2	-	±2.8
GF 7648	0.76	0.67	0.82	0.82	0.74	0.73	
% C.O.V.		±12.	±7.9	±7.9	±2.6	±3.9	±6.9
GF 7654	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	
% C.O.V.		±0.	±0.	±0.	±0.	±0.	±0.
GF 7675	4.41	4.35	5.44	4.35	3.50	-	
% C.O.V.		±1.4	±23.	±1.4	±21.	-	±11.7

F. Analytical Data from Gas Chromatography/Mass Spectrometry (GC/MS).

At the conclusion of Phase II, Task A--Laboratory Analysis of Soil and Water Samples by EC/GC--a meeting was held at the EPA Southeastern Environmental Research Laboratory in Athens, Georgia, which involved Mr. Don Brown, Mr. Bill Loy, and Dr. Anna M. Yoakum. After a careful review of the EC/GC data, the two samples containing the highest concentration of Aroclor 1254 were selected for further study utilizing gas chromatography/mass spectrometry (GC/MS). One sample selected was from the original excavation area, and the other came from below the surface of an area undisturbed in the original excavation. The two samples selected for evaluation were correlated to an actual sample of the askarel involved in the 1973 spill.

The GC/MS data outputs consist of total ion current chromatograms and specific ion searches of the data (for ions characteristic of the indicated polychlorinated biphenyls). The chromatograms obtained (Figures 9-13) show that the same isomers are present in the same ratios in the environmentally aged sample extracts and in the askarel. These data indicate that no selective degradation of the Aroclor 1254 isomers has occurred. Mass spectra typical of four, six, and seven chlorine biphenyls are presented in Figures 14-16.

VII. FATE OF POLYCHLORINATED BIPHENYLS (PCBs) AND POLYCHLOROBENZENES AFTER A TWO-YEAR EXPOSURE IN A NATURAL ENVIRONMENT

The experimental evidence presented in the preceding section of this report will now be evaluated in an effort to determine the fate of askarel after a two-year exposure in a natural environment. This evaluation will be conducted in two parts. The first part deals with PCBs and the second with the polychlorobenzene solvent. Only one commercial mixture of PCBs, Aroclor 1254, was found associated with the spill. Data evaluation for PCBs will, therefore, be restricted to this material.

Potential mechanisms for the loss of the askarel remaining in the spill area after the cleanup include volatilization, leaching, metabolic and nonmetabolic degradation. Each of these mechanisms and any other loss pathway which appears appropriate will be considered in conjunction with the experimental evidence collected.

A. Fate of Aroclor 1254.

1. Distribution of Aroclor 1254 In and Around the Spill Site in 1975. Aroclor 1254 was detected in 68 of 145 core samples collected in and around the 1973 excavation areas. Concentrations ranged from 0.05 to 67 mg/kg in the positive samples. A concentration distribution of Aroclor 1254 in the core samples is shown in Figure 17.

In order to effectively evaluate the 1975 distribution of Aroclor 1254, pertinent facts relative to the spill itself need to be considered. The magnitude of the 1973 spill and the elevation contours of the semi-mountainous terrain of the spill site assured an initial mass flow transport process which resulted in complete saturation of the

Figure 9. Total Ion Current Chromatograms

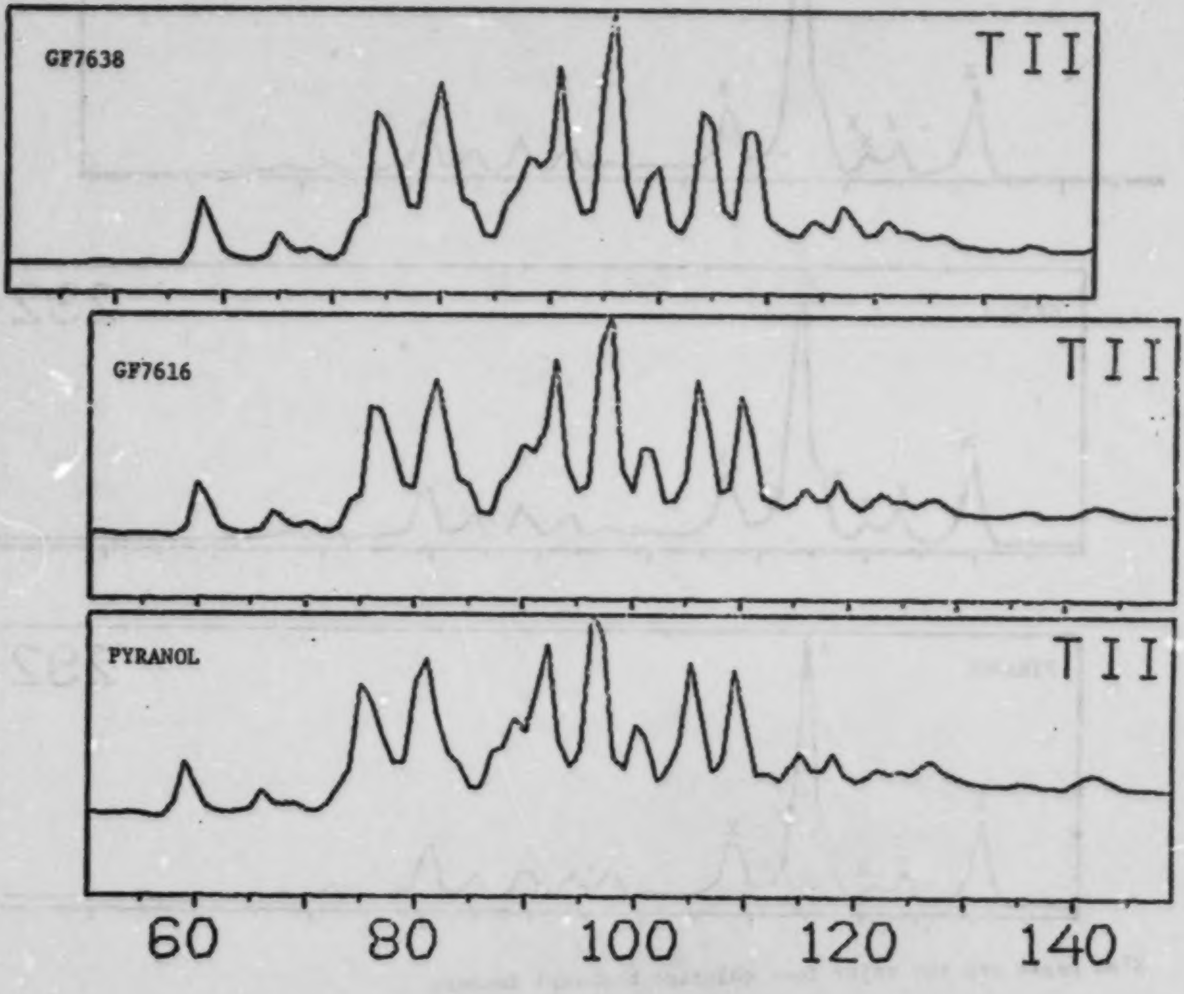
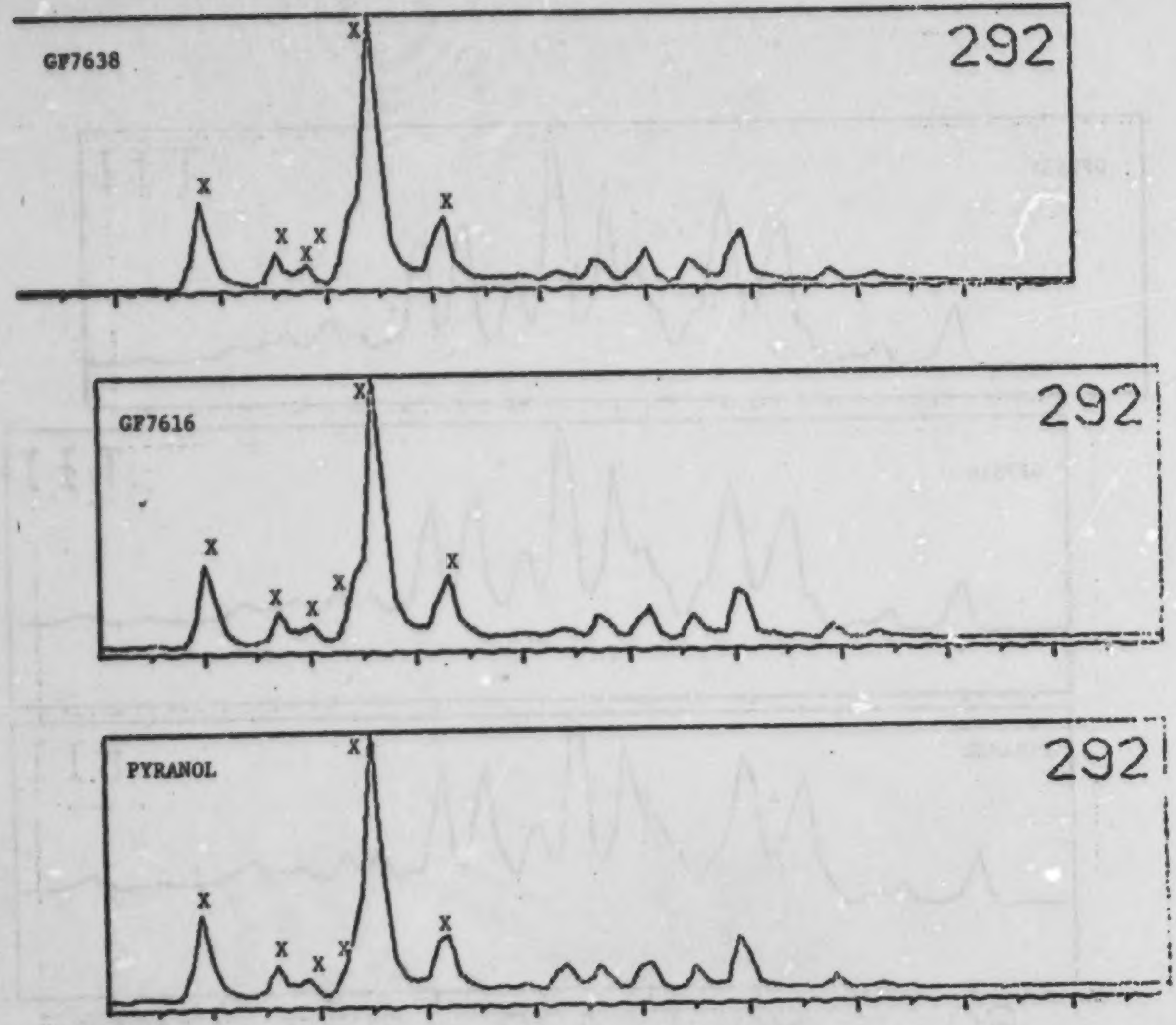
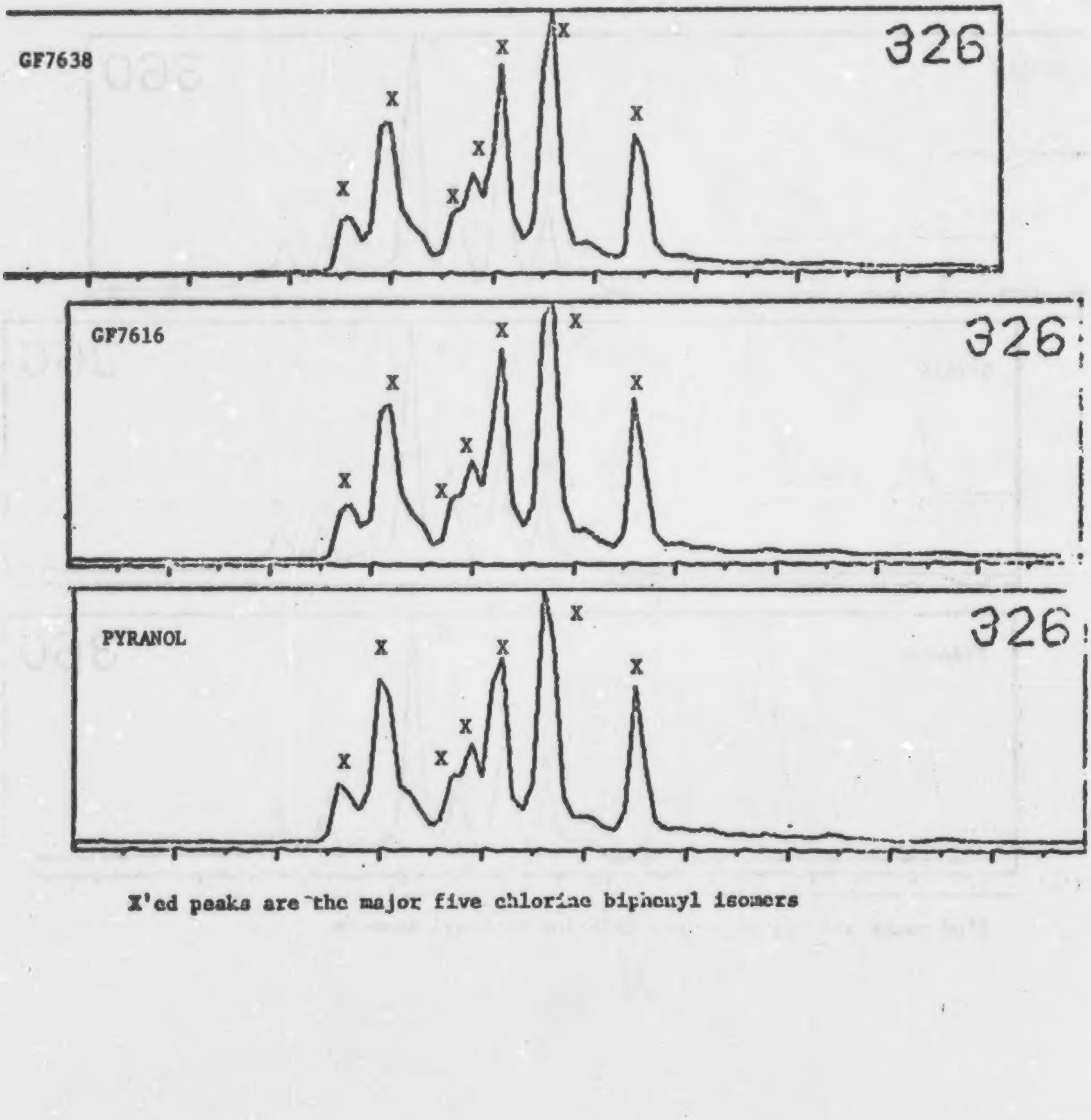


Figure 10. Specific Ion Search for the 292$^+$ Ion Indicative of the Four Chlorine Biphenyl Isomers



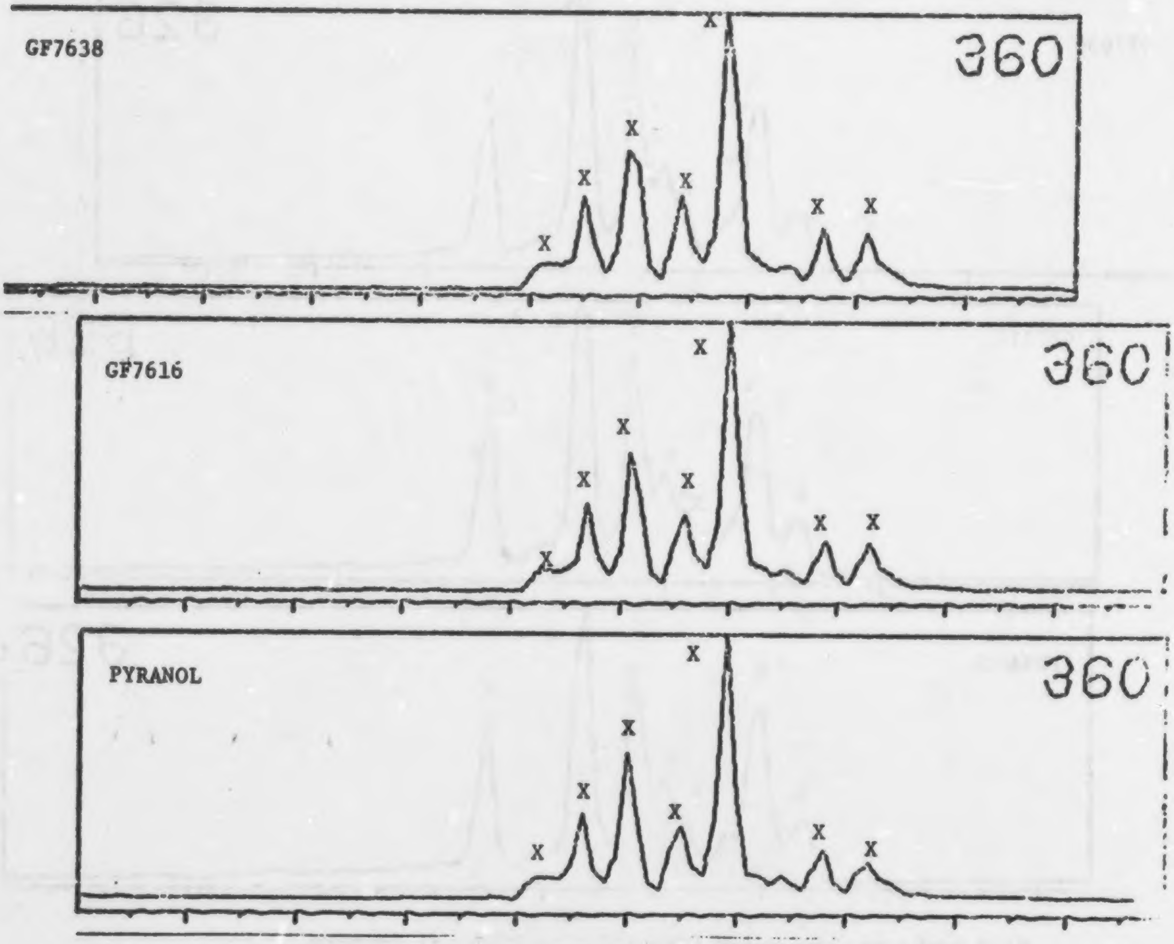
X'ed peaks are the major four chlorine biphenyl isomers

Figure 11. Specific Ion Search for the 326^+ Ion Indicative of the Five Chlorine Biphenyl Isomers



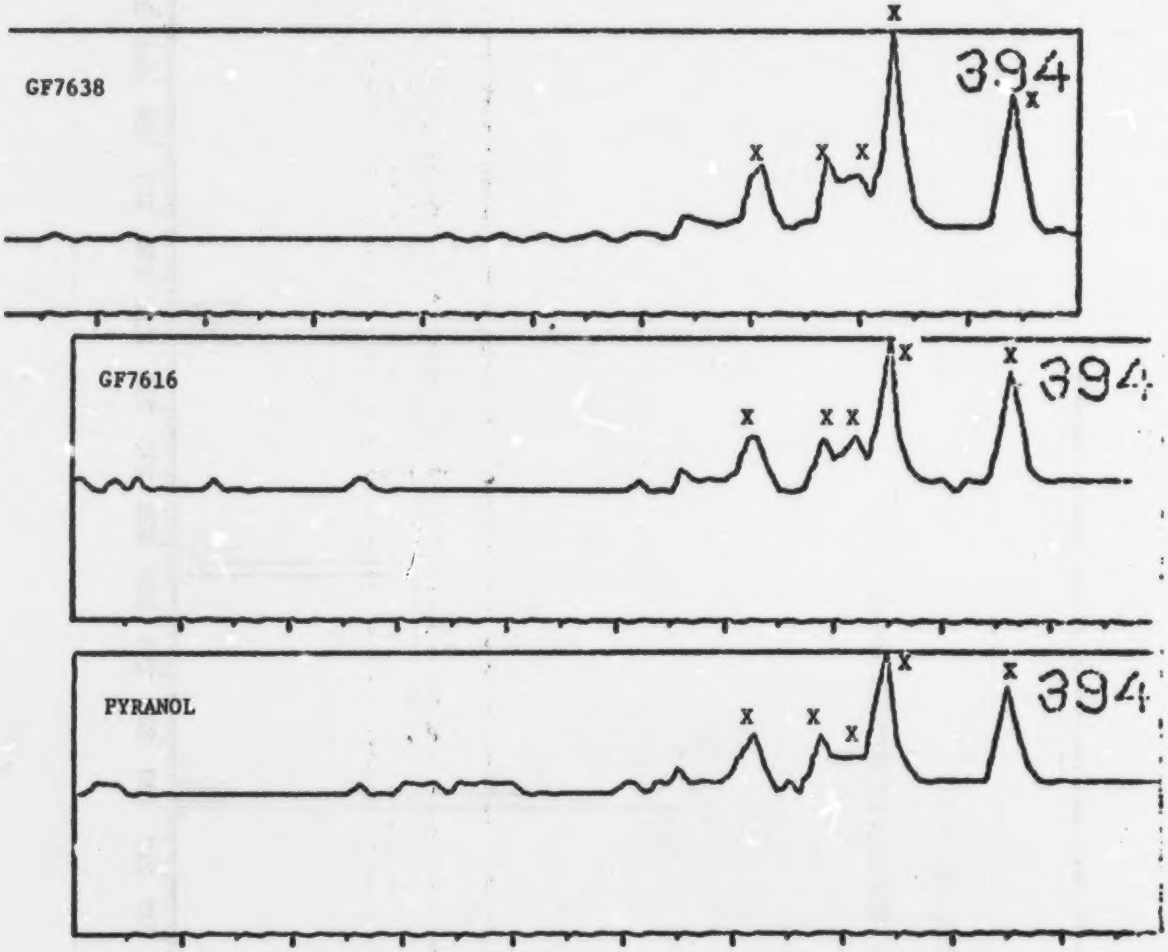
X'ed peaks are the major five chlorine biphenyl isomers

Figure 12. Specific Ion Search for the 360^+ Ion Indicative of the Six Chlorine Biphenyl Isomers



X'ed peaks are the major six chlorine biphenyl isomers

Figure 13. Specific Ion Search for the 394^+ Ion Indicative of the Seven Chlorine Biphenyl Isomers



X'ed peaks are the major seven chlorine biphenyl isomers

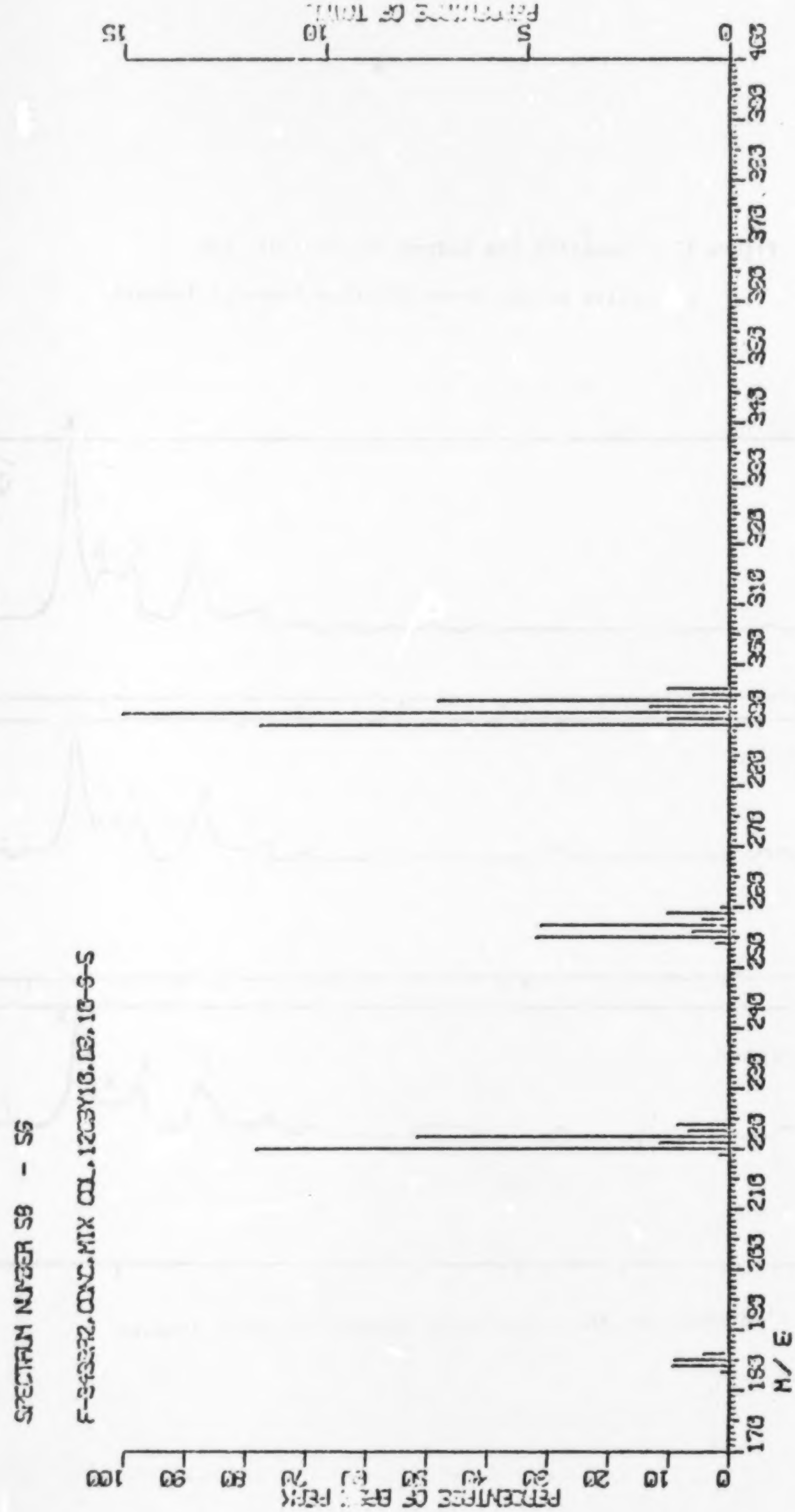


Figure 14. Spectrum typical of four chlorine Biphenyl

Figure 15. Spectrum typical of six chlorine Biphenyl

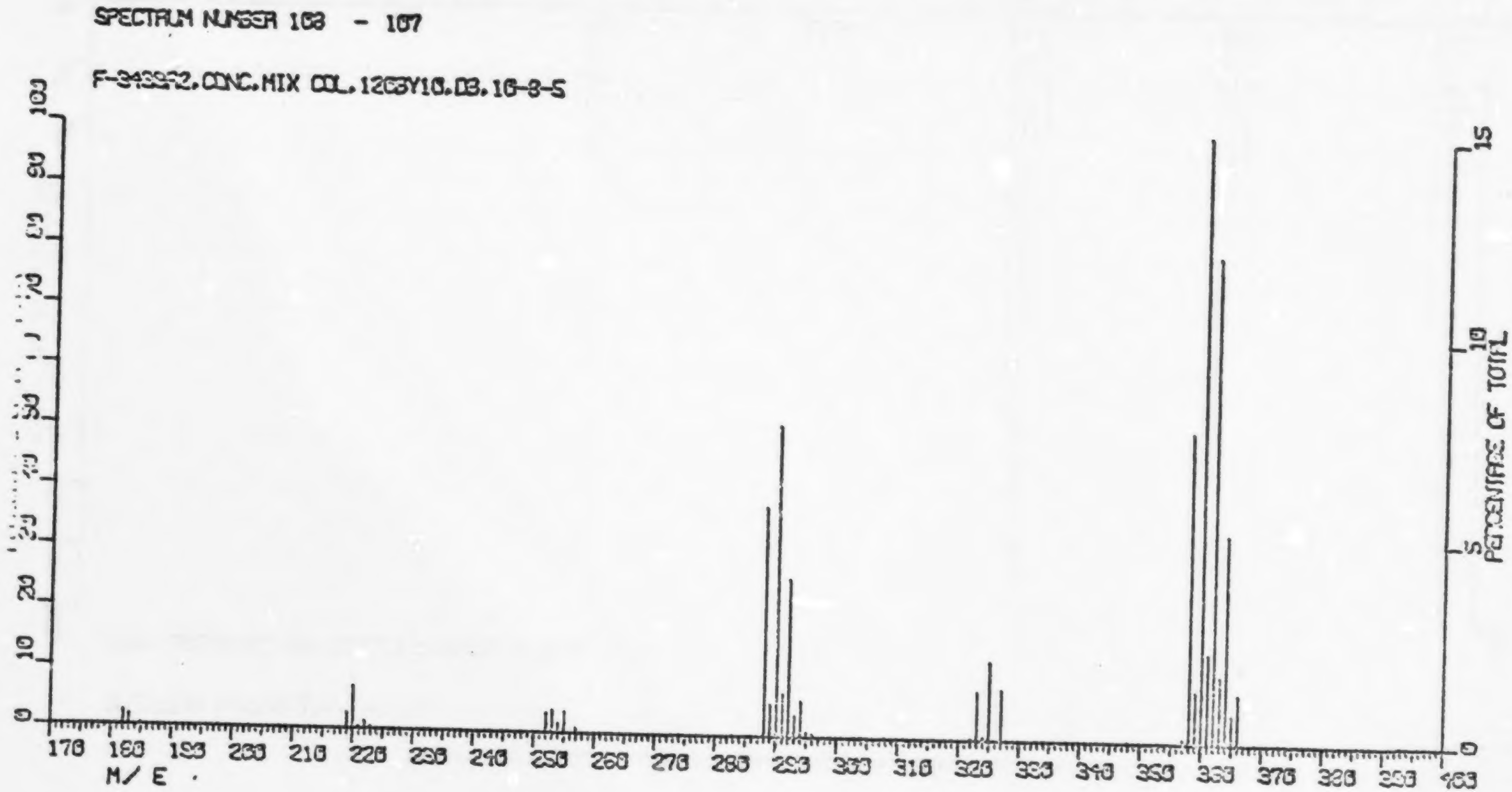
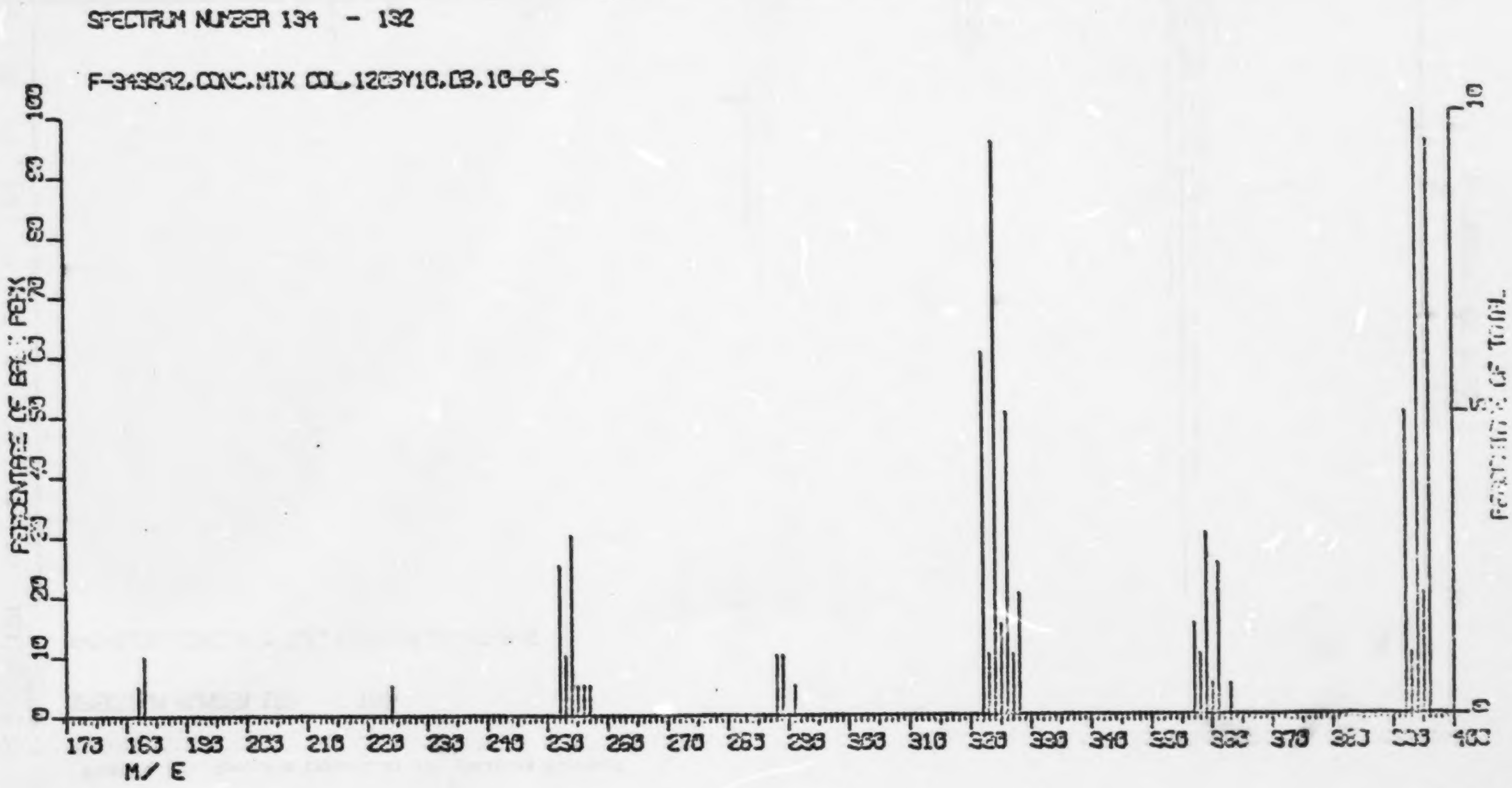


Figure 16. Spectrum typical of seven chlorine Biphenyl



top soil with varying degrees of penetration into the clay overburden. This transport process covered a relatively large area in both horizontal and vertical directions. The spread of the askarel was also affected by the movement of contaminated surface water resulting from massive rainfall in the weeks immediately following the spill. Excavation operations revealed that the distribution in the clay was non-uniform; and numerous so-called "hot spots" resulted from movement along the root systems of plants and trees, as well as from movement in the fractured chert frequently found in the clay matrix.

Based on 1973 data, three test core sites--RL, UC, and JF--were selected for the initial phase of the study. Concentration-depth profiles relating the 1975 data to the original 1973 data are shown in Figures 18-20. As was typical of the 1973 distribution, one so-called "hot spot" was detected; but the magnitude of the Aroclor 1254 was not excessive (<25 mg/kg). A comparative tabulation of 1973 and 1975 core data are given in Table 21.

One stated purpose of the study was to determine if a reduction in concentration of Aroclor 1254 in the soil had occurred either as a result of migration from the spill area or from degradation. By direct comparison, the 1973 data is higher in 61% of the locations; but the order of

Figure 17.

Concentration Distribution of Aroclor 1254 in Core Samples, 1975

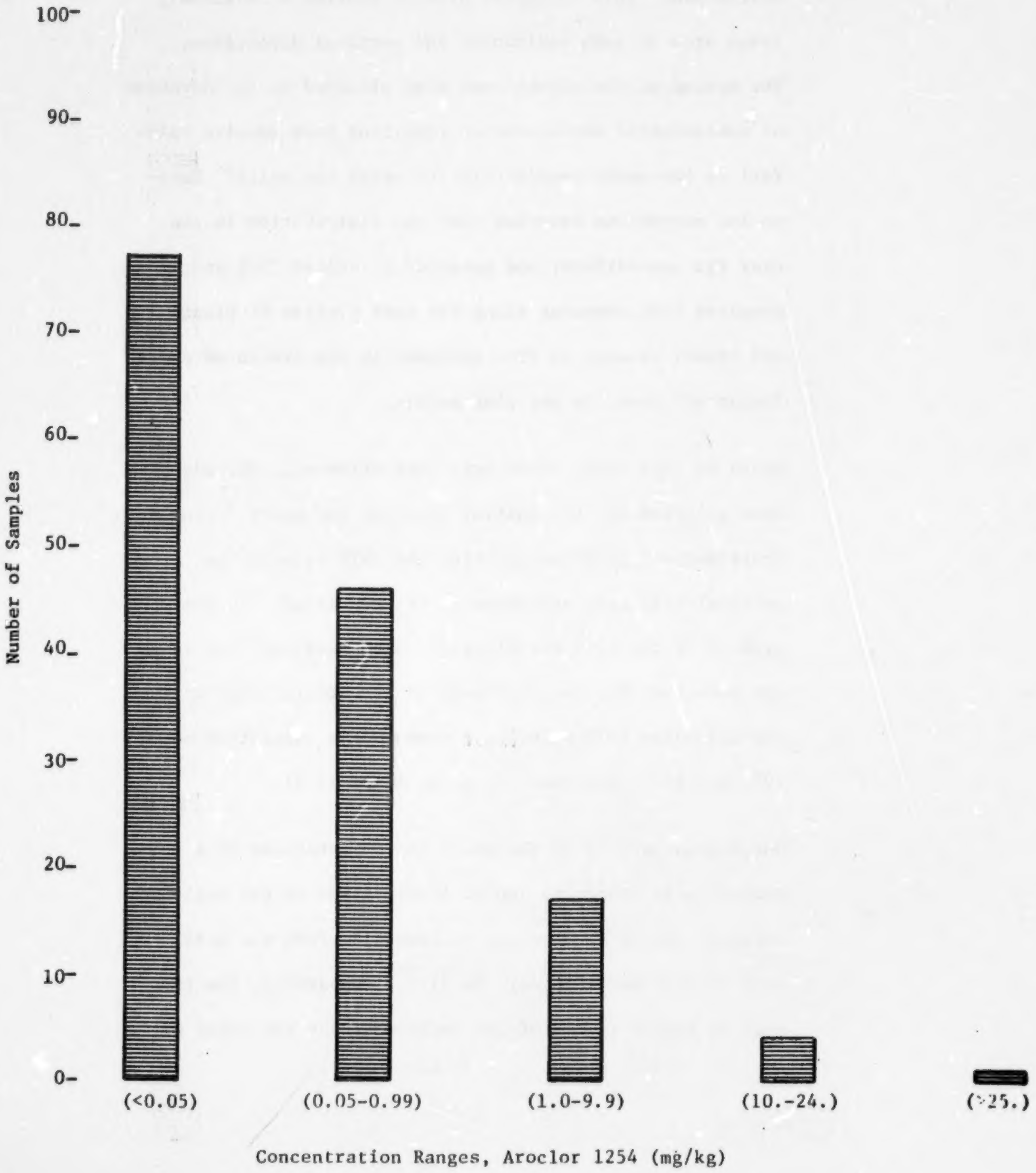


Figure 18. Concentration-Depth Profiles of Core Site UC, 1973-1975

Core depth profiles given in inches

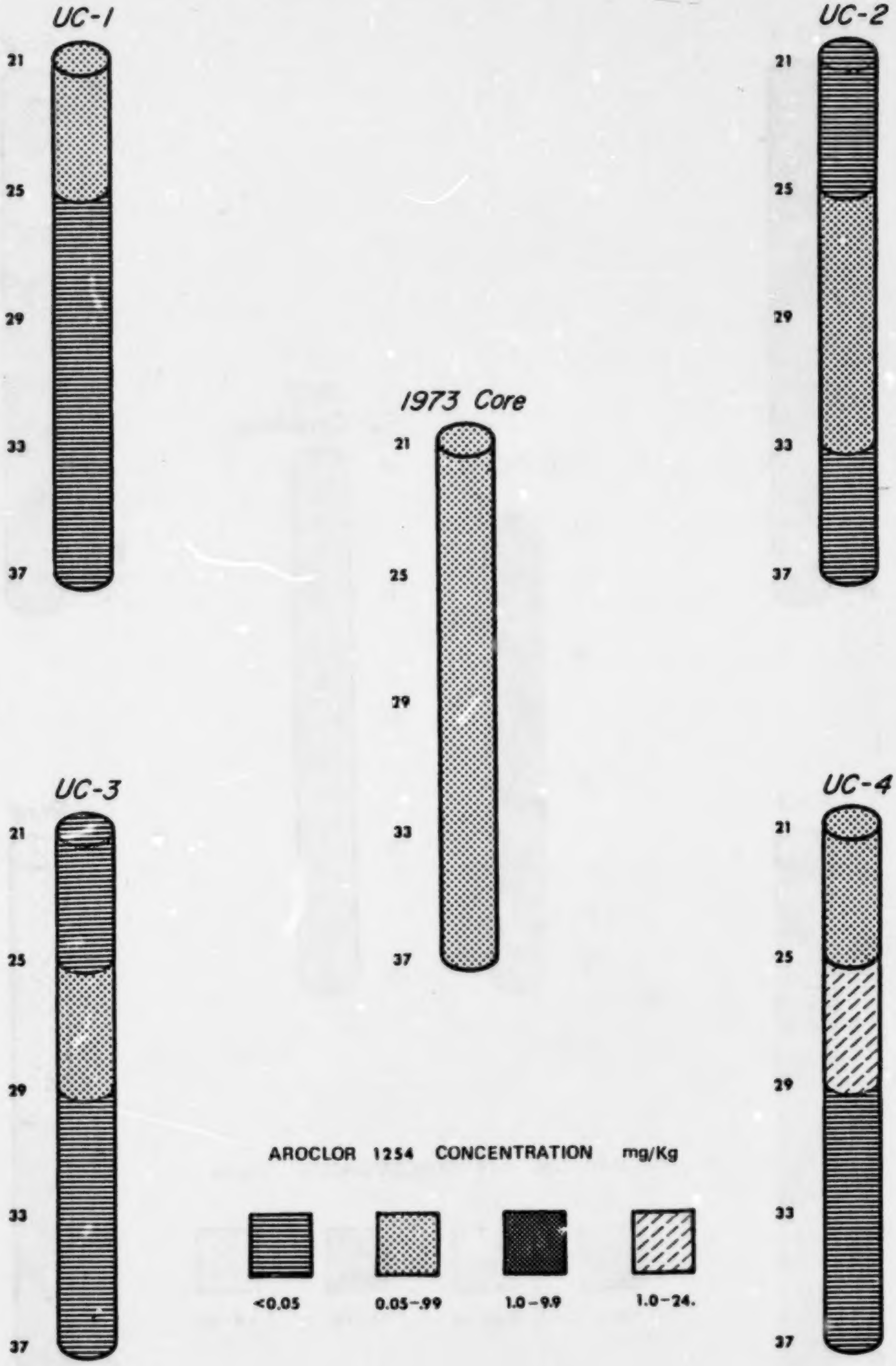


Figure 19. Concentration-Depth Profiles of Core Site RL, 1973-1975

Core depth profiles given in inches

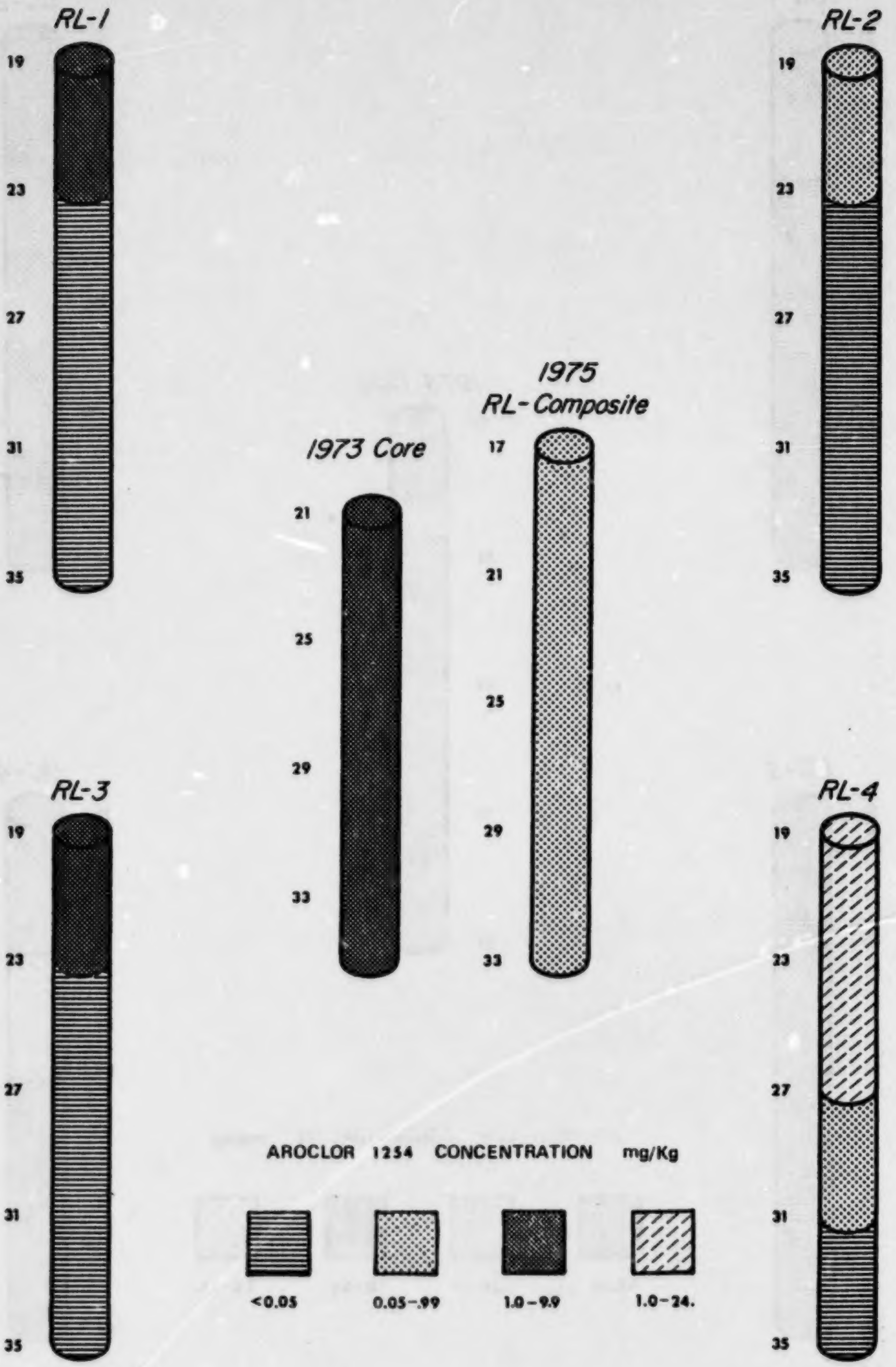


Figure 20. Concentration-Depth Profiles of Core Site JF, 1973-1975

Core depth profiles given in inches

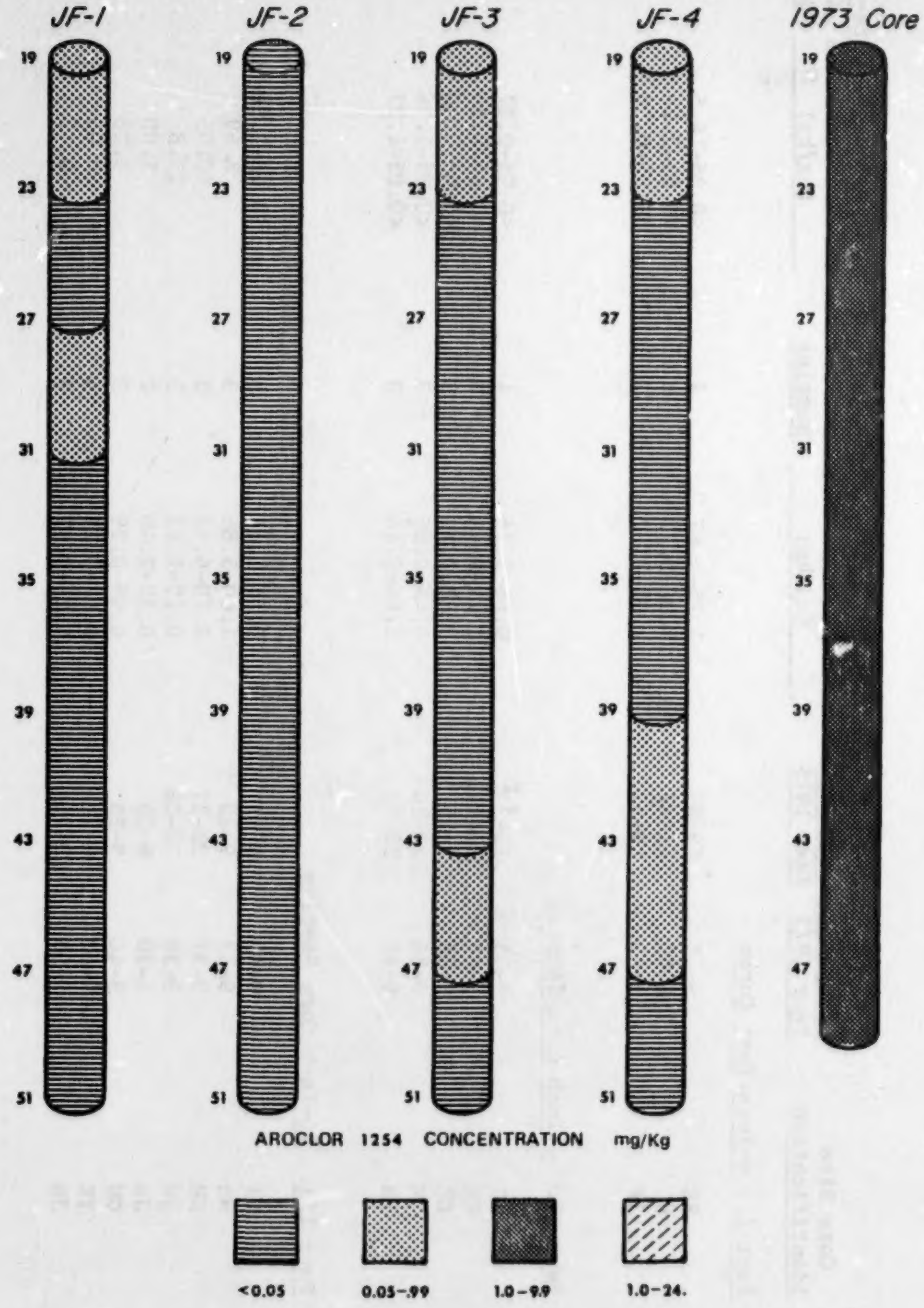


Table 21. Comparison of Analytical Data from Core Samples Collected in 1973 and 1975

Core Site Identification	Collection Depth Ranges (in Inches)		Analytical Results--1973		Analytical Results--1975	
	Year 1973	Year 1975	PCB Concentration (mg/kg)	No. of Samples	PCB Concentration (mg/kg)	No. of Samples
Part I. 4-Inch Test Cores						
RL	9-35	19-35	1.25-5.87	3	<0.05-14.5	17
UC	9-60	21-37	0.06-0.27	4	<0.05-2.24	16
JF	9-45	19-51	2.04-7.67	3	<0.05-0.36	32
Part II. 4-Inch Core Samples						
EK	9-35	15-31	0.86-2.76	4	<0.05-0.27	4
SR	9-45	9-41	0.27-0.43	3	<0.05-0.89	8
CC	9-36	9-25	0.88-2.20	3	<0.05-0.40	4
SM	9-36	20-36	0.44-0.85	3	<0.05-1.10	4
FM	9-66	33-65	1.64-3.44	3	<0.05-1.27	8
Part III. 16-Inch Core Samples						
LJ	9-43	9-41	0.55-1.45	3	<0.05-7.36	2
MB	9-37	9-25	1.60-5.86	3	3.69	1
KH	9-37	21-37	4.10-6.56	3	<0.05	1
SW	9-30	12-28	0.19-1.42	3	23.8	1
JR	9-20	9-25	0.52-2.40	2	5.00	1
GW	9-40	9-25	0.09-0.29	3	3.23	1
TE	9-62	9-25	0.07-0.21	4	<0.05	1
JD	9-35	9-25	0.27-0.82	3	0.17	1

Table 21. Comparison of Analytical Data from Core Samples Collected in 1973 and 1975 (continued)

Core Site Identification	Collection Depth Ranges (in Inches)		Analytical Results--1973		Analytical Results--1975	
	Year 1973	Year 1975	PCB Concentration (mg/kg)	No. of Samples	PCB Concentration (mg/kg)	No. of Samples
MM	9-66	9-73	0.23-6.72	4	<0.05-0.27	4
GE	9-35	19-35	0.68-2.32	3	0.32	1
CT	3-6	3-19	0.12	1	0.16	1
MT	9-40	9-41	1.37-3.00	3	0.89-4.35	2
BT	9-36	9-41	3.44-311.	3	1.34-10.1	2
LP	3-6	3-19	3.26	1	3.41	1
JS	3-6	4-20	3.85	1	5.62	1
FA	9-42	9-41	1.85-8.50	3	<0.05	2
PT	3-6	3-19	0.50	1	66.6	1
FO	9-36	9-41	0.05-0.21	3	<0.05	2
AA	6-9	3-19	0.60	1	0.34	1
EL	9-50	9-41	0.11-1.00	3	<0.05	2
PS	0-18	2-9	0.09-0.69	3	2.04	1
DV	9-34	9-25	0.21-0.58	3	<0.05	1
SS	9-36	9-41	0.46-5.70	3	<0.05	2
HH	9-66	9-41	<0.05-1.35	3	0.12-0.67	2
AM	9-38	9-25	0.09-0.15	3	<0.05	1
VT	3-6	0-16	0.72	1	0.17	1
JE	39-45	29-45	0.16-0.20	2	<0.05	1
BA	34-37	21-37	0.12	1	<0.05	1
TR	33-41	25-37	<0.05	2	<0.05	1
CV	33-52	33-45	<0.05-1.39	4	<0.05	1
PQ	9-22	9-25	0.40-0.44	2	0.21	1
MD	0-18	3-19	0.76-7.50	3	0.15	1
BS	9-48	10-58	0.27-15.8	4	0.13-7.45	3
HT	9-55	9-41	0.13-4.80	4	<0.05-0.16	2
ZZ	9-40	9-41	0.47-7.50	3	0.29-0.50	2
BR	0-18	3-19	0.63-6.00	3	0.91	1
SL	9-61	9-25	<0.05-0.20	3	2.05	1

magnitude for the Aroclor 1254 concentrations are comparable for both years; and no significant migration patterns are observed.

2. Degradation of Aroclor 1254. Two possible degradation modes exist--metabolic and nonmetabolic. Each degradation mechanism will now be considered from the standpoint of applicability to the system under study.

a. Chemical Transformation--The non-biological alteration of a chemical introduced into any part of the environment is dependent on the moisture, pH, and temperature of that environment; on the nature of reactive groups on the agent; and on the presence of catalytic sites. In addition, the nature and intensity of available illumination determines photochemical reactions.

Irradiation (photolysis) of Aroclor 1254 under laboratory conditions has produced dechlorinated products; and, in the presence of air and water, hydroxylated and hydrated products have been identified in the polar products of the irradiation. Although these theoretical routes for chemical degradation exist, the extreme stability (chemical inertness) of Aroclor 1254 coupled with the absence of illumination at the potential reaction site make chemical transformation a highly improbable degradation mechanism.

b. Biological Alteration--By analogy to the dechlorination of DDT to DDD by soil microorganisms, biodegradation of Aroclor 1254 is considered to be a possible degradation mechanism in a natural environment. The unique biochemical asset of certain aerobic microorganisms to catalyze early steps in degradation allows for the formation of metabolites which can enter the common pathways of metabolism. The establishment of measureable biodegradation is dependent on the ease of physical or chemical sequestration of the PCB components due to the structure of the molecule as it relates to microbial enzymatic action. The intrinsic toxicity of the askarel, environmental factors affecting microbial populations and their specificity, and available time for the maximum development of the degradation process are also significant considerations in the interpretation of biological alterations of PCBs.

c. Aroclor 1254 Degradation Assessment--Aroclor 1254 is a mixture of chlorinated biphenyl homologs. If no degradation in the environment occurred, or if all homologs degraded at the same rate, the ratio of homologs in "aged environmental samples" should be the same as that in the askarel introduced into the environment at the time of the spill. On the other hand, if the homolog ratio in the "aged environmental samples" from the spill site differs from that of the askarel spilled, some process(es) must be operating in the environment to remove different homologs at different rates. According to data supplied by the Monsanto Company (35), the typical percent (w/w) composition of Aroclor 1254 is similar to that given in Table 22.

All chromatograms from the EC/GC analyses of 1975 samples were carefully examined for peak alterations and for the appearance of new peaks with reference to the chromatogram of the askarel released into the environment at the time of the spill. Comparative chromatograms for Aroclor 1254 in a typical "aged environmental sample" and Aroclor 1254 in the askarel spilled in 1973 are shown in Figure 21. By comparing the two chromatograms, it is readily apparent that the ratio of homologs in the "aged environmental sample" is the same as that in the askarel introduced into the environment at the time of the spill. These results indicate that either there has been no degradation in the environment or that all homologs have degraded at the same rate.

Using gas chromatography-mass spectrometry (GC/MS), the homolog distribution of selected 1975 samples was compared to the distribution exhibited in a sample of askarel from the 1973 spill. These data also confirm that the ratio of homologs in the "aged environmental samples" is the same as that of the askarel spilled in 1973.

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(35) Monsanto Company, "Presentation to the Interdepartmental Task Force on PCBs," Washington, D. C., May 15, 1972.

Table 22. Typical Homolog Composition of Aroclor 1254 (35)

Homolog (No. of Chlorine/biphenyl)	Aroclor 1254*
0	<0.1
1	<0.1
2	<0.5
3	1.
4	21.
5	48.
6	23.
7	6.
8	ND†

*Percent (w/w) by GC/Mass using area correlation factors by homolog response.

†ND = None Detected, <0.01%.

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(35) Monsanto Company, "Presentation to the Interdepartmental Task Force on PCBs," Washington, D. C., May 15, 1972.

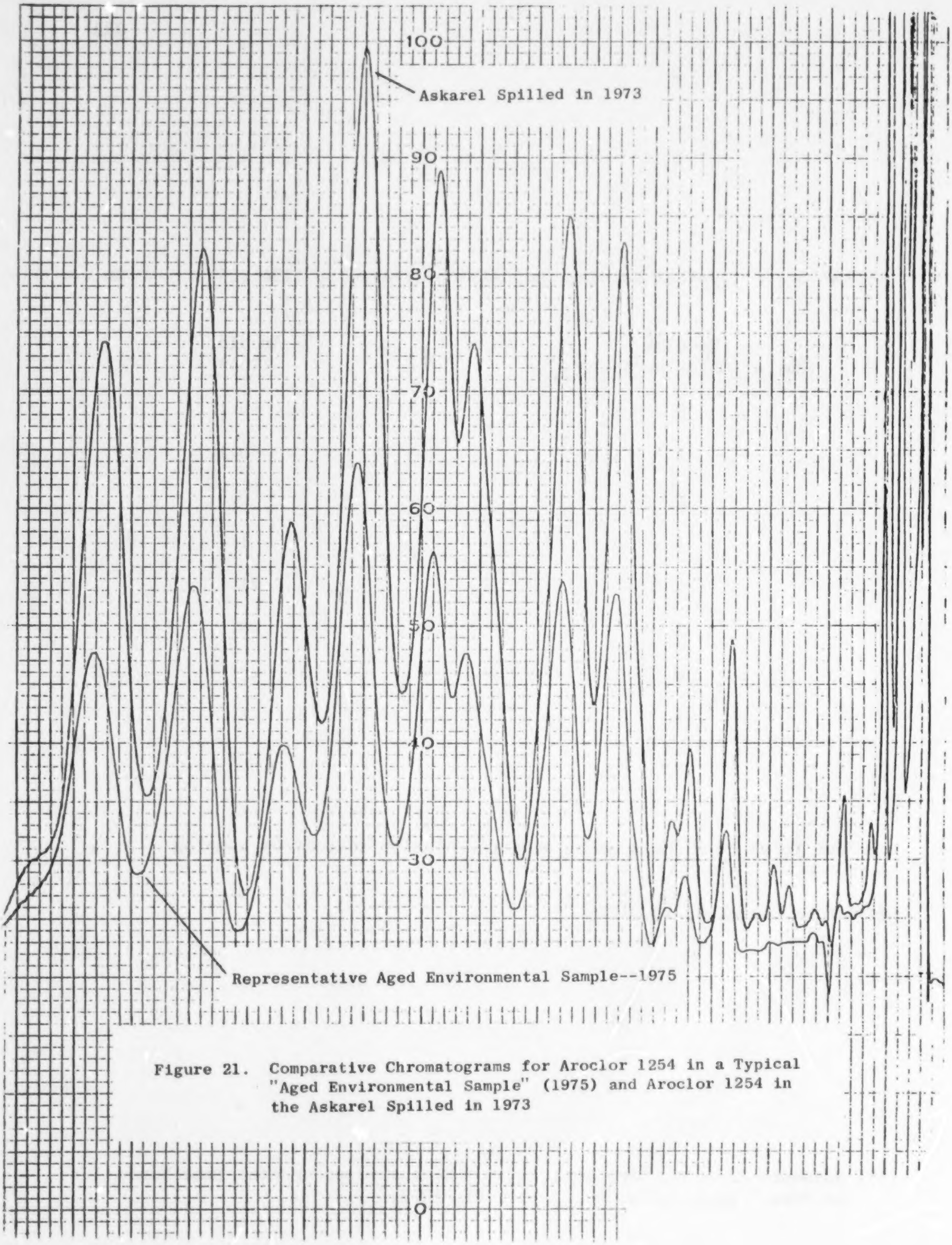

Figure 21. Comparative Chromatograms for Aroclor 1254 in a Typical "Aged Environmental Sample" (1975) and Aroclor 1254 in the Askarel Spilled in 1973

No evidence was found by GC/MS and/or EC/GC to indicate the presence of degradation products in any of the "aged environmental samples" collected in or around the spill site. Primary biodegradation can be defined as minimum alteration of the chemical structure of the material in question to an extent that characteristic properties of the original material are no longer evident. Based on the experimental evidence collected, and considering the definition just presented, it may be concluded that no detectable reduction in the concentration of Aroclor 1254 in the soil has occurred as the result of chemical transformation or biodegradation. An evaluation of the occurrence of major soil microorganisms is consistent with this conclusion in that the three microbial groups studied were probably not present in sufficient numbers to support measureable degradation of the PCB.

B. Fate of Askarel Solvent.

The scope of this project did not include the analysis of soils for the askarel solvent. Only water samples, collected adjacent to the study area, were included to provide information on the rate of intrusion of polychlorobenzenes into ground water. As a consequence, since biodegradation analyses were limited to soil samples, an assessment of solvent degradation is not possible. This discussion of the so-called "fate" of askarel solvent in the spill environment will be limited to the distribution of polychlorobenzenes in ground water adjacent to the spill site.

The 1973 data showed only minimal movement of Aroclor 1254 in the ground water. Only two ground water sampling stations gave positive data for Aroclor 1254. These locations were a spring just below the spill area and a well less than one hundred feet from the spill excavation area. The highest Aroclor 1254 concentration detected in a water sample was 2.1 ppb.

Migration of the askarel solvent, however, was completely different from that observed for the PCB, Aroclor 1254. Differential migration of the askarel solvent in the spill environment was observed in a well water sample collected March 22, 1973. A subsequent screening of selected water sources--wells, creeks, ponds, etc.--revealed an interesting phenomenon. There were two distinct patterns for the solvent concentration in the water samples. One closely resembled the component distribution of the askarel solvent spilled. The other was almost 95% trichlorobenzenes.

Because of this observed phenomenon, a selected number of representative core drillings at the spill site were analyzed for askarel solvent. These data indicated that tetra-and pentachlorobenzene were preferentially retained in the soil while the other solvent components--especially the trichlorobenzenes--had selectively moved out of the area. This study also showed that Aroclor 1254 was preferentially retained in the soil. Data from monitoring programs confirmed that water samples with solvent patterns resembling the askarel solvent component distribution indicated possible contamination by surface water run-off and seepage of surface water into a supply. Water with the high trichlorobenzene concentrations indicated intrusion of these solvent components into the ground water supply. A graphic representation of solvent concentration in the well located closest to the spill site is shown in Figure 22. Samples from this station collected during the follow-up study still show solvent present in the water at the 1.0 ppb concentration level.

These data clearly indicate that the more water-soluble components of the askarel solvent invaded the ground water supply almost immediately after the occurrence of the spill. Leaching was the migration mechanism responsible for the intrusion of the lower chlorinated benzenes into the ground water supply.

Based on the 1973 and 1975 data, it can be concluded that intrusion of lower chlorinated benzenes into a ground water supply used for drinking water purposes occurred rapidly after the spill. This same water supply contains minimal, but detectable, quantities of askarel solvent two years after the occurrence of the spill.

C. Over-all Assessment of the Environmental Impact of the Spill.

The contractor did not observe the spill area prior to the actual spill; however, observations began on March 21, 1973,

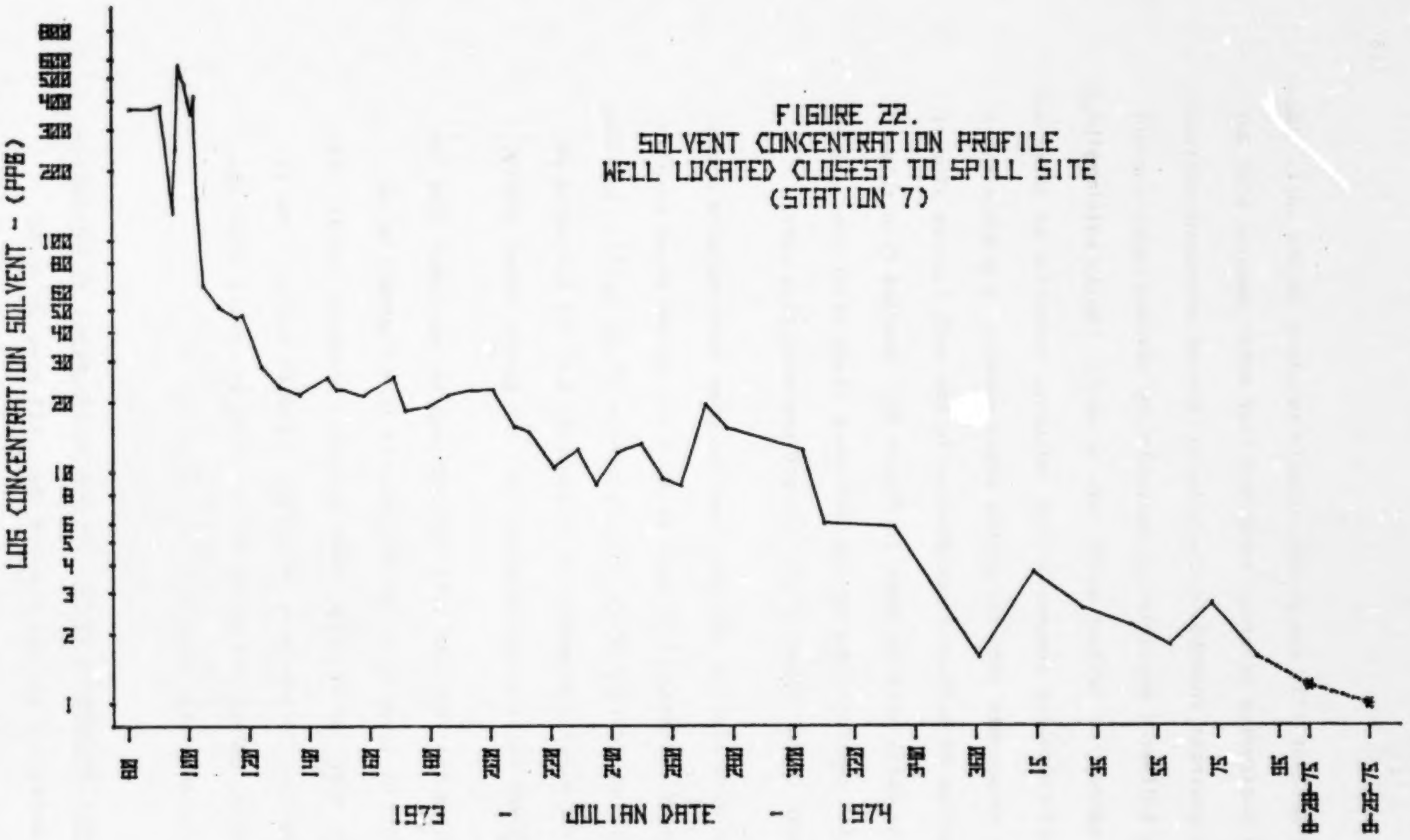

FIGURE 22.
SOLVENT CONCENTRATION PROFILE
WELL LOCATED CLOSEST TO SPILL SITE
(STATION 7)

approximately two and one-half weeks after the spill occurred. Invasion of the spill area by workers and heavy equipment involved in the cleanup had already transpired by this time. There had been heavy rainfall during the two and one-half week period immediately after the spill. The area received 12.44 inches of precipitation during the month of March which constituted a 7.23 inch departure from the norm. All assessments will utilize, as an environmental basis, the condition of the area at the time the contractor arrived.

1. Condition of the Area Immediately After the Spill.

   a. Primary Spill Area--The primary spill area was located adjacent to the intersection of a main north-south highway and a secondary access road utilized mainly by residents living in sparsely developed areas along the lake (see Exhibit I). The property on which the spill occurred was a segment of land designated for pasture farming.

   The spill site is situated in a watershed approximately 0.6 mile long which drains into the lake in a northeasterly direction and generally runs parallel to the secondary access road. The distance from the spill site to the lake is approximately 0.5 mile. The main watershed also received drainage from several secondary watersheds adjacent to it. The spring well, Station 1B, is located approximately 0.2 mile from the spill site in this north-east trending hollow. Most of the chemical spilled migrated down the slope toward the north-east, influenced primarily by the surface topography.

The primary spill area, which was later excavated, covered an area approximately 250 feet long and 125 feet wide. This area was sparsely wooded with pines and hardwoods including: Shortleaf Pine (*Pinus echinata*), Eastern White Pine (*Pinus strobus*), Virginia Pine (*Pinus virginiana*), White Oak (*Quercus alba*), Southern Red Oak (*Quercus falcata*), Mockernut Hickory (*Carya tomentosa*), and Flowering Dogwood (*Cornus florida*). Natural understory plant associations were observed in the area at this time. Two Southern Red Oaks and a Shortleaf Pine with base diameters of 12-18 inches were removed from the excavation area in 1973.

Although the cleanup operation was not intended in any way to be a terrestrial ecology study, cursory observations were made on the biota of the immediate spill area and the surrounding area at various times during the period of March through July, 1973. No mammals, reptiles or amphibians and very few birds were observed in the vicinity at this time. Crustacea (crayfish) were observed, and watercress blanketed the area of the spring well (Station 1B). There was some evidence of damage to trees and understory plants in the area of heaviest contamination.

b. Area Peripheral to Spill Site--It was suspected that the chemical may have also migrated to the south-east across the road and into another watershed. South-east from the crest of the hill where the spill occurred the topography is gently rolling through fields and wooded areas down to the lake. The distance from the spill site to the lake in this direction is approximately 0.4 mile. Little wildlife was observed in this area. Evidence of wildlife within pastured segments including dry weather ponds was absent.

2. Condition of Spill Area - August 1975.

In 1973, the cleanup procedure resulted in extensive excavation in the spill area. Contaminated soil was removed; and the excavated areas were sealed, backfilled, and packed with uncontaminated soil. The entire affected area was covered with top soil, seeded with grass, and landscaped. This area had received little maintenance since 1973; and, as a result, grass and weeds were overgrown, hindering field operations. A rotary mower was used to cut the overgrowth, and the area was raked.

According to the property owner, several damaged trees had been removed in the period between the 1973 cleanup operation and the latest study.

Again, the 1975 follow-up study was not intended to examine the terrestrial ecology of the area; however, over a period of approximately one month (July and August, 1975), observations made in the spill area indicated no obvious detrimental effects to any biota of the ecosystem. In the course of sampling, several specific observations were made. Crayfish and minnows were found in abundance in the spring well waters, as were various aquatic insects and plants. The immediate spill area was infested with insects including ants, spiders, ticks, grasshoppers, crickets, flies, mosquitoes, bees, and yellow jackets. Several garter snakes were seen in this area also. Segmented worms were observed in core samples taken within a few feet of the surface.

APPENDIX

Method for Analysis of Water and Sediment for Polychlorinated Biphenyls

Monsanto Company

Analytical Chemistry--Method 69-13

February 1970

ANALYSIS OF WATER AND SEDIMENT FOR POLYCHLORINATED BIPHENYLS

SCOPE

This methodology was developed for the determination of the amount and type of polychlorinated biphenyls (PCB) in water and sediment samples. Absolute confirmation of PCB structures is not obtained with this method. Structure proof can be obtained using additional techniques such as mass spectrometry to further identify the GC fractions.

PRINCIPLE

The PCB(s) in water and sediment samples are extracted into an organic solvent. Interfering components are then removed from the extracts by chemical treatment and column adsorption chromatography. The amount and type of PCB present is determined by electron capture gas chromatography (EC/GC).

REAGENTS

Hexane	Nanograde, Mallinckrodt Chemical Works, Catalog No. 4159.
Acetonitrile	Nanograde, Mallinckrodt Chemical Works, Catalog No. 2442.
Sodium Sulfate	Anhydrous, granular: AR grade, Mallinckrodt Chemical Works, Catalog No. 8042. Heat at 400°C for one hour prior to use.
Alumina Adsorption	(for chromatographic analysis) 80/200 mesh, Fisher Scientific Co., Catalog No. A540. Heat at 400°C for a minimum period of 4 hrs. and deactivate with 5% (w/w) distilled water. Alumina column preparation: Fill a chromatographic column with hexane up to the point where the reservoir joins the column and push a glass wool plug to the bottom with a glass rod. In a 50 ml beaker measure 35 ml of deactivated alumina (∿30g), and pour this slowly into the column. Tap or vibrate the column to settle the alumina and top the alumina with 2-3 cm of anhydrous sodium sulfate. Wash the column with 50-100 ml of hexane prior to the addition of the sample.

Distilled Water	Extracted with hexane to remove hexane soluble electron capturing impurities.
Sulfuric Acid	Analytical Reagent Grade, SG = 1.84
Potassium Hydroxide	Analytical Reagent Grade
Ethanol	Formula 2B
2.5% (w/v) Alcoholic Potassium Hydroxide	Dissolve ∿ 12.5 grams of AR grade KOH in 500 ml of ethanol
9/1 (v/v) Sulfuric Acid - Water	Carefully add 270 ml of AR-grade sulfuric acid to 30 ml of distilled water in a 500 ml iced beaker
PCB Standards	Aroclor 1242, 1248, 1254, and 1260

APPARATUS

1. Separatory funnels equipped with ground glass stoppers and Teflon stopcocks: 125, 250, 500, 1000 and 2000 ml capacities.
2. Kunderna-Danish Evaporative Concentrators, 500 ml capacity equipped with 3-ball Snyder columns and graduated 5 ml capacity vials: Ace Glassware Company, Catalog No. 6707.
3. Chromatographic columns, glass, 10" x 20 mm (OD) with a 5" x 50 mm (OD) reservoir at the top, equipped with Teflon stopcocks.
4. Sintered glass filter funnels, 600 ml capacity, 90M.
5. Flat bottomed boiling flasks, 125 ml capacity: Ace Glassware Company, Catalog No. 6896, Code - 04.
6. Liebig Condenser, 200 mm in length: Ace Glassware Company, Catalog No. 5915, Code - 12.
7. Hot plates, Corning PC-100: Fisher Scientific Company.
8. Water bath, Thelco, Precision Scientific, Model No. 84, Fisher Scientific Company.
9. Reciprocating variable speed shaker, Eberback Corporation, Fisher Scientific Company.
10. 10 µl Hamilton Syringes, Catalog No. 701N.
11. 32 oz. all glass mortars and pestles.

12. 8 x 12 x 2" (2-1/2 qt.) Pyrex baking dishes.

13. U. S. Standard Sieve, No. 30, Fisher Scientific Company.

14. Usual laboratory glassware.

SAMPLING

It is to be assumed that a rather wide variety of sampling techniques were employed in collecting the samples submitted for analysis. In general the procedures used were probably selected for ease of adaption to the local situation. For this reason water and sediment samples were usually treated as follows:

Water

Where possible the entire water sample, including the container in which it was collected, was extracted with hexane. With larger samples, where this was not physically possible, the containers were simply agitated and a 250 ml portion used for analysis.

Sediment

Any excess water was decanted and the entire sediment transferred to a glass baking dish to air dry at room temperature. The dried material was transferred from the dish into a mortar and pestle and ground. The ground sediment was sieved, remixed, and a 250g portion taken for analysis.

PROCEDURES

Extraction of Water Samples

1. Extraction of water samples - after agitating, transfer the entire aqueous sample or a 1000 ml aliquot into a graduated glass cylinder. Record the volume of the sample and quantitatively transfer it to a separatory funnel with distilled water.

2. Rinse the graduated cylinder with one 50 ml portion of hexane and add each to the separatory funnel.

3. Stopper the separatory funnel and shake vigorously for at least 2 minutes. Allow the layers to separate and transfer the lower aqueous phase to a second separatory funnel.

4. Extract the water sample a second time with a 50 ml portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous layer to the original separatory funnel.

5. Repeat the extraction with a third 50 ml portion of hexane. Discard the aqueous layer and combine the hexane extracts.

6. Filter the combined extracts through a 4" funnel plugged with glass wool which is covered with sodium sulfate. Collect the filtrate in a Kunderna-Danish evaporative concentrator, add a small boiling chip, put the Snyder column in place, and reduce the hexane volume to less than 5 ml by heating the apparatus in a 80-90°C water bath. (CAUTION: SOLVENT VAPORS MUST BE VENTED TO A HOOD.)

7. After cooling, remove the 5 ml graduated tube and transfer hexane extract to an alumina adsorption column washing it in with several 5 ml portions of hexane.

8. Carefully add 100 ml of hexane to the column reservoir and collect the total eluent in either a 250 ml volumetric flask or a Kunderna-Danish evaporative concentrator.

9. If the column eluent is collected in a volumetric flask, dilute to volume with hexane and proceed with the gas chromatographic analysis.

10. If the column eluent is collected in a Kunderna-Danish evaporative concentrator, reduce solvent volume, cool, dilute to volume and proceed with the gas chromatographic analysis.

Extraction of Sediment and Soil Samples

1. Decant off any excess water and transfer the entire sediment sample to a glass baking dish. Air dry at ambient temperature (heat should not be applied).

2. When dry, transfer the soil/sediment to a mortar and pestle and grind. Sieve the ground material through a No. 30 mesh sieve and weigh 250g (to the nearest 0.01g) into a 16 oz. narrow neck screw cap (aluminum foil liner) glass bottle.

3. Moisten the soil with water (∿ 10 ml) and add 150 ml of acetonitrile. Cap the bottle tightly, and mechanically shake for a minimum period of 1 hour.

4. Quantitatively transfer the acetonitrile extract into a 600 ml sintered glass filter funnel containing a 1/4" layer of anhydrous sodium sulfate. Collect the filtrate in a 600 ml beaker (vacuum filtration may be necessary).

5. After the acetonitrile has completely drained into the beaker, wash the bottle twice with 50 ml portions of acetonitrile, adding each wash to the funnel after the previous has completely percolated through the sediment.

6. Quantitatively transfer the extract to a Kunderna-Danish evaporative concentrator, add a small boiling chip, put the Snyder column in place, and reduce the solvent volume to less than 5 ml by heating the apparatus in a 80-90°C water bath. (CAUTION: SOLVENT VAPORS MUST BE VENTED INTO A HOOD.)

7. After cooling remove the 5 ml graduated tube and transfer the concentrate of extracts to a 125 ml extraction flask with the aid of several small portions of solvent.

8. Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen and add 25 ml of 2.5% alcoholic potassium hydroxide.

9. Add a boiling chip, put a water condenser in place, and allow the solution to reflux for 45 minutes.

10. After cooling, transfer the solution to a 250 ml separatory funnel with the aid of 25 ml of distilled water.

11. Rinse the extraction flask with 25 ml of hexane and add it to the separatory funnel.

12. Stopper the separatory funnel and shake vigorously for at least 1 minute. Allow the layers to separate and transfer the lower aqueous phase to a second separatory funnel.

13. Extract the saponification solution with a second 25 ml portion of hexane. After the layers have separated add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.

14. Repeat the extraction with a third 25 ml portion of hexane. Discard the saponification solution and combine the hexane extracts.

15. Carefully add 25 ml of the sulfuric acid solution (9:1 concentrated sulfuric acid/water) to the hexane extracts.

16. Stopper the separatory funnel and shake vigorously for at least one minute. Allow the layers to separate and discard the lower aqueous-acid layer. Repeat this step until the acid layer is colorless.

17. Wash the hexane with 25 ml portion of water. Discard the water wash.

18. Filter the hexane extract through a 4" funnel plugged with glass wool which is covered with a layer of sodium sulfate into a Kunderna-Danish evaporative concentrator.

19. Add a small boiling chip, put the Snyder column in place and reduce the hexane volume to less than 5 ml by heating the apparatus in a 80-90°C water bath.

20. After cooling, remove the 5 ml graduated tube and transfer the hexane extract to an alumina adsorption column washing it in with several 5 ml portions of hexane.

21. Carefully add 100 ml of hexane to the column reservoir and collect the total eluent in either a 250 ml volumetric flask or a Kunderna-Danish evaporative concentrator.

22. If the column eluent is collected in a volumetric flask, dilute to volume with hexane and proceed with the gas chromatographic analysis.

23. If the column eluent is collected in a Kunderna-Danish evaporative concentrator, reduce solvent volume, cool, dilute to volume and proceed with gas chromatographic analysis.

Electron Capture Gas Chromatographic Procedure

Instrument: F&M 402 Biomedical Gas Chromatograph
Detector: High Temperature Ni^{63} Electron Capture Cell
6 mm x 6' Glass Column, 4% XE-60 on 80/100 mesh
Chromosorb W, HP, AW-DMCS

Column Temperature: 160°C
Detector Temperature: 300°C
Injection Port Temperature: 195°C
Pulse: 150

Flow Rates
Helium Carrier ∿ 60 ml/min
Argon-Methane Purge ∿ 120 ml/min

Using EC/GC as the determinative step, inject in duplicate 1-10 μl of each solution into the chromatograph. By comparison with standard solutions injected, in duplicate, under the same operating conditions, determine the amount and type of Aroclor using the individual or total peak height method.

The electron capture detector should also be used to guide the isolation procedures. Water and sediment extracts can be checked for the presence of PCBs and/or interferences by injecting μl portions of the extracts at various points in the extraction and concentration schemes. In this manner, it can be determined if the sample needs to be concentrated or diluted and if the clean up procedures should be employed.

DISCUSSION

Extraction

The extraction of PCB's from water employing hexane as the extractant was found to be quantitative and to be sufficiently simple and rapid for use as a routine procedure.

The evaluation of this method was based on spiking water samples with standard acetone solutions of PCB's. The spiking method consisted of adding the PCB's in acetone (25-50 µl) to 500 ml of tap water in a 32 oz. narrow neck screw cap jar. After thoroughly mixing, duplicate 225-250 ml aliquots were taken and subjected to the proposed sample preparation and work up as outlined. The results were quantified by preparing a calibration curve using standard hexane solutions of the PCB's used to spike the water samples. The major isomer peak height was used to construct the calibration plot.

The average recovery and deviation achieved substantiated the applicability of the method for the quantitative recovery and analysis of PCB's from water at the ppb-ppm level.

No PCB recovery experiments from spiked sediment and soil samples have been performed. Instead, several of the residual solids representative of some of the types of sediment or soil analyzed were re-extracted with hexane/acetone (40/60) in a soxhlet extractor to test for the efficiency of the acetonitrile extraction step. The hexane, after isolation by dilution with distilled water was then carried through the purification steps. Recoveries by soxhlet extraction have indicated that the acetonitrile extraction of PCB's was essentially quantitative in the cases checked.

Sample Concentration

Concentration of sample extracts is necessary, prior to clean up by chromatographic or chemical means, to reduce sample size and increase sensitivity. The preferred method of concentrating allows minimum loss through volatilization or chemical decomposition and requires a minimum time. The three methods of solvent volume reduction most commonly used are evaporation by exposure to a stream of air, evaporation employing a Kunderna-Danish evaporative concentrator equipped with a Snyder column, and evaporation under reduced pressure. We have used all three techniques and have not encountered any significant losses from volatilization or chemical alternation. However, the Kunderna-Danish evaporative concentrator and the stream of air were employed because of the ease of use.

Column Adsorption Chromatography and Chemical Clean Up

Silica gel, Florisil and Alumina deactivated with 0, 1.0, 1.5, 2.0 and 5% water were investigated as adsorbants for the elimination of interferences. Alumina (5% water) was found to be more effective and reproducible than either silica gel or Florisil. The activity of alumina varies with age and lot, therefore, 5% water was added to the alumina, after heating for a minimum of 4 hours at 400°C to insure a reproducible activity.

Saponification and subsequent extraction of the sample with sulfuric acid is an effective way to remove a number of chlorinated hydrocarbon interferences as well as other matrix interferences. PCB's are not affected.

Electron Capture Gas Chromatography

Columns:

Column performance is the key to effective gas chromatographic analysis and as such the choice of column materials is particularly important. Ideally, the support employed should be inert, mechanically strong, and of high surface area. For these reasons, Chromosorb W, HP, AW-DMCS was used in all of our work.

A variety of polar and non-polar liquid phases were investigated. The following columns were found to provide adequate separation, etc., for use in PCB analysis by electron capture: 4% (w/w) DC-200, SF-96, OV-17, SE-30, SE-54, XE-60, Apiezon L, and 6% QF-1. DC-200 and XE-60 or QF-1 have been found to be the most suitable of these liquid phases.

Another important consideration when working with an extremely sensitive detector and consequently low levels of materials is column conditioning. With polar phases such as XE-60 and QF-1, we have found that operating a new column overnight at a temperature 25-50°C higher than to be used during analysis results in a more stable column. A no-flow conditioning technique is employed to condition non-polar columns. The column is purged with carrier gas, heated for 30 minutes at an elevated temperature without carrier flow and then cooled to room temperature. At the end of this cycle the carrier flow is resumed and the conditioning is completed as in the case of the polar liquid phase. Two precautions: during conditioning, the column should not be connected to the detector and one should not exceed the maximum safe temperature of the liquid phase.

Since all liquid substrates bleed to one degree or another and columns eventually degrade, we characterize all new columns with two column performance indicators - the number of theoretical plates (N) and a tailing factor (T). p,p'-DDT is employed to check these parameters because it is known to degrade on "poor" columns. In this manner, we can determine if the performance of a new column is satisfactory and when the column performance begins to fall off. We consider a column good if the number of theoretical plates per foot is on the order of 400-500 with tailing factors of 1.0-1.3. Calculation of these parameters is shown in the Appendix. Additionally, there should be no significant extraneous peaks upon injection of a pure p,p'-DDT standard.

Other chromatographic conditions that can be adjusted are column temperature and flow rates. Although resolution of a mixture increases with decreasing temperature, a temperature should be chosen that allows the elution of all components within a convenient time period. The temperatures given are optimum for 42% chlorinated biphenyl, temperatures are increased when specifically analyzing for the higher chlorinated biphenyls, i.e., 54%, 60%, etc. The flow rates are optimum for our instrument, column and detector system and, of course, should be adjusted if better results can be achieved.

Two gas chromatographic systems have been used for PCB analysis - F&M Model 402 and 5750. We find that any system of instrument and column suitable for chlorinated pesticides is satisfactory for PCB analysis. The bulk of analyses in our laboratories was carried out using the system outlined. The use of the high temperature Ni^{63} electron capture cell is highly recommended. The ability to operate at higher temperatures prevents maintenance problems due to contamination from high boiling components. Glass columns should also be employed.

Detection and Measurement:

Quantitative determinations employing the electron capture detector are non-stoichiometric measurements made by comparing peak heights or areas for known concentrations with those for unknown compositions. Except for sharp peaks, peak area measurements are usually more reproducible than peak height measurements but are extremely time consuming unless a recording integrator is employed. However, peak height measurements are as accurate as disc integration of triangulation and if the peak shape represents a gaussian curve, the height may be considered independent of the base. Three variations of the peak height quantification procedure were employed.

Case I	EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with no evidence of interferences.
Case II	EC gas chromatogram of PCB unknown altered with respect to standard PCB with no evidence of interferences.
Case III	EC gas chromatogram of PCB unknown unchanged with respect to standard PCB with evidence of interference.

The amount of PCB's in Case I samples were determined by preparing a plot of the major peak height vs. concentration; for Case II, a plot of the total sum of all major peaks vs. concentration. With Case III samples, a peak free from interference was used. When dominant interferences were present, one or more of the chemical clean up procedures was employed.

In all cases, the response of the electron capture detector must be linear for quantitative analysis. With our instrument any response less than 50 at an attenuation of 8 x 10 fell into the linear response range at a pluse rate of 150. This corresponds to approximately 5 x 10^{-9}g of Aroclor 1242.

Contamination:

In determining PCB's in water, soil and sediment by electron capture gas chromatography, laboratory sources of contamination can be a major problem. The samples and extracts should never be allowed to come in contact with materials other than glass, Teflon or metal. Laboratory glassware should be thoroughly washed with hot, soapy water, rinsed with distilled water, acetone, and then hexane. All equipment should also be rinsed again with hexane just prior to use and blanks should be frequently carried through all steps of the procedures to insure against the possibility of contamination.

SENSITIVITY	Two parts per billion Absolute sensitivity - 0.5×10^{-9} grams Volume injected - 5 µl. Final volume of extract - 5 ml. Sample size - 250 ml.

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